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Selective determination of thidiazuron herbicide in fruit and vegetable samples using molecularly imprinted polymer fiber solid phase microextraction with ion mobility spectrometry detection (MIPF-SPME-IMS)

R. Mirzajani [a,*], Z. Ramezani [b], F. Kardani [a]

[a] Chemistry Department, Faculty of Science, Shahid Chamran University of Ahvaz, Ahvaz, Iran
[b] Department of Medicinal Chemistry, School of Pharmacy, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

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ABSTRACT

In this study, we use corona discharge ion mobility spectrometry (CD-IMS) as a detection technique for determining thidiazuron (TDZ) after its selective microextraction using molecularly imprinted polymer (MIP) fibers. This is the first time that MIP fiber solid phase microextraction-ion mobility spectrometry (MIPF-SPME-IMS) was used to detect TDZ. The fiber was synthesized simply using a narrow bore silica capillary as a mold by the copolymerization of methacrylic acid–ethylene glycol dimethacrylate imprinted with TDZ. The prepared MIPs were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM). The obtained flexible MIP monolithic fibers have high chemical and thermal stabilities with good selectivity to TDZ. The effective parameters influencing the polymerization were also investigated. In addition, the influences of different factors such as pH, extraction time, desorption solvent, and temperature on the extraction efficiency of the analyte were investigated. Under the optimum conditions, analytical parameters such as linearity, precision and limit of detection were also evaluated. The linear range was in the range of 0.01–20 μg L^{-1} (r^2 = 0.9980) and the limit of detection was 0.005 μg L^{-1}. Intra- and inter-day precisions were satisfactory with a relative standard deviation (RSD) of 0.9% and 2%, respectively. Finally, the established MIPF-SPME-IMS method was successfully applied in the selective determination of TDZ residues in fruit and vegetable samples.

1. Introduction

Plant growth regulators (PGRs), which are important herbicides used in applications to plant culture media, comprise five main classes including auxins, gibberellins, ethylene, abscisic acids, and cytokinins (CKs) [1,2]. Most of these PGRs are naturally produced in plants, where they regulate growth or destroy undesired elements in plants. Synthetic PGRs are widely sold for use in agriculture due to their low price and greater stability than the natural homologs [3,4]. These synthetic herbicides, which exhibit physiological activity similar to that of the natural pesticides and plant hormones, can effectively promote, inhibit, or modify the growth and development of plants [5]. Some PGRs appear to have been extensively used on edible plants in many countries [6]. Thidiazuron (TDZ: [1-phenyl-3-(1, 2, 3-thidiazol-5-yl) urea]), having the structure shown in Fig. 1A, is among the most active cytokinin-like growth substance in the tissue culture of woody plant species [7]. However, residues have been reported in some environmental materials, such as water, soil, cotton seed, and fruits and vegetables [8]. Therefore, the development of a readily applicable method for residual analysis is necessary. Few analytical assays reported in the literature describe a method for analyzing TDZ residues in fruit and vegetable samples. These include liquid chromatography-tandem mass spectrometry (LC-MS/MS) [1], dispersive liquid-liquid microextraction using liquid chromatography with time-of-flight mass spectrometry (LC-TOFMS) [2–4] and liquid chromatography (LC) with UV detection systems (LC-UV) [9,10]. Usually, these standard methods have good selectivity due to their use of powerful separation techniques. However, most of these procedures are laborious, time-consuming, expensive, and environmentally unfriendly. Modern trends in analytical chemistry are moving toward the simplification and miniaturization of sample preparation procedures, as well as the minimization of solvent and reagent consumption [10–12]. Solid-phase microextraction (SPME) has proved to be an efficient and sensitive method for the extraction and pre-concentration of target analytes in a broad range of applications [13]. Generally, SPME exhibits a flexible extraction ability by changing various fiber coatings. To date, a variety of sorbent-coated SPME fibers have been applied in environmental, toxicology, drug, and biomedical analysis [14–19]. However, commercial polymer-coated SPME fibers are fragile and extra care must be taken

* Corresponding author.
E-mail address: rmirzajani@scu.ac.ir (R. Mirzajani).

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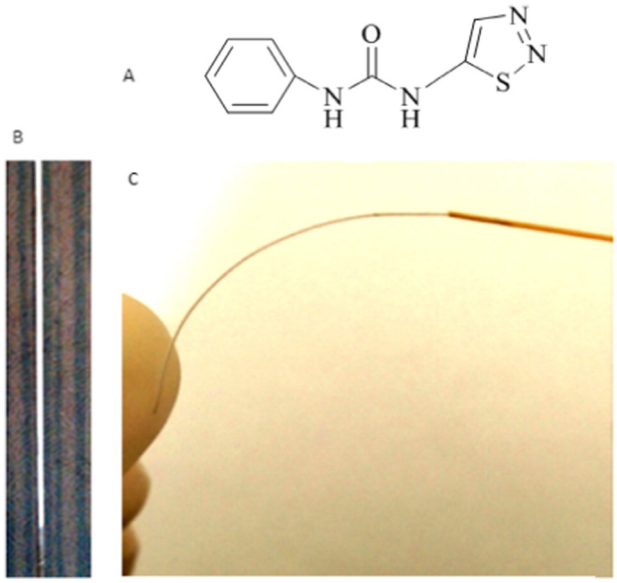

Fig. 1. A) Structure of thidiazuron ($C_9H_8N_4OS$, MW: 220.25), prepared MIP fiber based on thidiazuron template B) before and C) after mechanical withdrawals from glass mold.

during their use. They generally face disadvantages relating to their nonresistance to high temperature, insufficient selectivity, breakage of the fiber, stripping of coatings, the possibility of swelling in some organic solvents, the limited number of reuse times, and relatively high cost [20]. Therefore, it is vital to develop low-cost SPME fibers that have high thermal and chemical stability, and more robust coatings having high selectivity for the extraction of different kinds of compounds. One of the materials used for this purpose has been molecularly imprinted polymers (MIPs). Imprinted fibers are prepared either by silylation of silica fibers following MIP coating [21–22] or by direct synthesis of the MIP fibers (monoliths) using fused silica capillary columns as molds, with the silica being etched away after polymerization [23]. Researchers are striving to develop analytical instrumentation to detect ionizable compounds with enhanced sensitivity, low cost, a fast analysis time, and good selectivity. Currently, ion mobility spectrometry (IMS) is one of the most widely used analytical techniques [24]. IMS is based on the gas-phase separation of ionized compounds under an electric field at ambient pressure by their mobility in the drift gas. Corona discharge has proved to be a nonradioactive ionization source in IMS and has been successfully used in detecting many compounds [25–27]. After ionization the ions are accelerated into a drift tube, where they collide with ambient air molecules leading to a measurable average drift velocity. As a separation technique, this can provide a resolution power similar to that of gas chromatography [28] and could be developed to provide separation capabilities at lower cost and with greater ease of operation. In this study, we fabricated a flexible MIP-SPME fiber using fused silica capillaries as molds and, for the first time, applied MIPF-SPME–IMS to simply, selectively and accurately determine the presence of TDZ on fruit and vegetable samples without any derivatization steps or any need to use chromatographic techniques.

2. Experimental

2.1. Reagents and standards

We obtained Thidiazuron ([1-phenyl-3-(1,2,3-thidiazol-5-yl) urea], $C_9H_8N_4SO$, TDZ, 99.9%) from Fluka (Buchs, Switzerland), and purchased methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA), and azo (bis)-iso butyronitrile (AIBN) from Sigma-Aldrich (St. Louis, MO, USA). All organic solvents (chloroform, ethanol, acetone, and acetonitrile) were high-performance liquid chromatography (HPLC grade) were purchased from Merck (Darmstadt, Germany). Doubly distilled water was used in all experiments. Standard stock solution containing a 500 mg L^{-1} concentration of analyte was prepared by dissolution in methanol and stored at 4 °C prior to use. Working solutions were obtained on a daily basis by diluting the stock solution with water to an appropriate extent. The sodium chloride, hydrochloric acid, sodium hydroxide, and phosphoric acid were analytical reagent-grade (Merck).

2.2. Ion mobility spectrometer

The ion mobility spectrometer (Isfahan, TOF Tech. Pars) used in this study was designed and constructed at Isfahan University of Technology, Iran, [29]. Briefly, the main components of this instrument include an IMS cell, two high voltage power supplies, a pulse generator, an analog-to-digital converter, and a computer to record spectra. The IMS cell, consisting of ionization and drift regions, is housed in a thermostatic oven in which the temperature can be adjusted from room temperature to 200 °C. The shutter grid consists of two series of parallel wires biased to a potential, which creates an orthogonal field relative to the drift field to block ion passage into the drift tube. The grid potential is removed for a short period of time by a pulse generator in order to admit an ion pulse into the drift region [26]. We used nitrogen as the carrier and drift gases with flow rates of 400 mL min^{-1} and 1000 mL min^{-1}, respectively. The instrument was equipped with a needle-to-plane corona discharge ionization source, as described by Tabrizchi et al. [30–31]. The needle voltage was independently adjustable. In all the experiments, the needle potential was kept constant to create a stable and steady corona. The default Faraday plate detector configuration consisted of a 21-mm-diameter stainless steel plate positioned approximately 1.0 mm behind the aperture grid. An analog to digital A/D converter (PicoScope, UK) was used and the digitized signal was averaged over a number of scans. All IMS spectra were obtained by data acquisition software and each IMS spectrum was the average of 50 individual spectra. We used a corona discharge ionization source with a positive mode in these experiments [32].

2.3. Sample preparation

Fresh fruit and vegetable samples (apple, kiwifruit, tomato, watermelon, and melon) were bought from local supermarkets in Ahvaz (Iran). About 200 g of each fruit or vegetable was chopped and homogenized in a food processor and the freshly pressed fruit juices were centrifuged at 4000 rpm for 5 min. Samples were then filtered using a Whatman No. 42 filter paper prior to analysis and stored at 4 °C in the dark. To extract the analyte from the sample matrices, 500-μL juice samples were transferred into 5 mL vials, diluted with double distilled water, and the herbicide was directly extracted from the solution using MIPF-SPME according to the proposed method. It was then submitted to the ion mobility spectrometer for further analysis. Samples were prepared in the same way described above, both with and without spiking with required amounts of TDZ.

2.4. Preparation of molecularly imprinted polymer and monolithic fiber

We prepared the monolithic fiber for the MIP according to a previously reported method by Djozan and Baheri [33–34]. First, 2.1 mmol of the template molecule (TDZ) was dissolved in 30 mL acetonitrile (porogen). Then, 30 mmol of the functional monomer (MAA), 120 mmol of the cross-linking monomer (EGDMA), and 280 mg of AIBN were added. Subsequently 1 mL of the mixture was transferred into a small glass tube and deoxygenized with a stream of nitrogen gas for 10 min. To prepare the monolithic fibers as a mold, we washed capillary home-made fused silica tubes, 4 cm in length and with an internal diameter of 0.3 mm, with methanol and dried them with a stream of nitrogen. Using a syringe, the capillary was filled with a polymerization mixture, previously degassed with a N_2 stream for 5 min, and