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Short communication

Pesticide analysis in tomatoes by solid-phase microextraction and micellar electrokinetic chromatography

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Abstract

The analysis of a group of seven pesticides (i.e. six fungicides: pyrimethanil, procymidone, nuarimol, fenarimol, benalaxyl and penconazole and one insecticide: pirimicarb) in tomato samples by micellar electrokinetic chromatography is investigated. For this purpose, reversed electrode polarity stacking mode and solid-phase microextraction (SPME) have been used as on-line and off-line preconcentration procedures, respectively. Tomato samples were first homogenized and extracted with acetone. After suitable evaporation and reconstitution of the extract in water, a SPME procedure using poly(dimethylsiloxane)/divinylbenzene fibers was used. Due to the strong influence of the sample matrix in the extraction, a matrix matched calibration of spiked tomato samples was developed. The method was found to be linear between 0.5 and 2.5 mg/kg. Limits of detection achieved are below the maximum residue limits established by the European Union and Spain legislation as well as by the Codex Alimentarius (except for penconazole). The potential of the method was demonstrated by analyzing 12 tomato samples (of ecological and non-ecological production) taken from regional cultivars. No residues of the selected pesticides were detected in any of the samples.

Keywords: Micellar electrokinetic chromatography; Pesticides; Reversed-electrode polarity stacking mode; Solid-phase microextraction; Tomatoes

1. Introduction

Tomatoes are one of the most widely grown vegetables in the world and also the most important item of the fruit and vegetables processing sector [1]. The long-term selection process imposed to improve tomato productivity and quality has made tomato crops less resistant to diseases, pests and adverse environmental conditions and, in order to maintain a high production yield, the use of pesticides is a conventional agricultural practice (as well as for other cultivars).

Capillary electrophoresis (CE) with its various modes of operations has proved to be very useful in the analysis of pesticides [2–4]; however, most of these applications are restricted to the separation of standards, mainly because of its lower sensitivity when compared to chromatographic techniques. Different on-column trace enrichment schemes (stacking or sweeping techniques) have been developed to overcome this limitation. Juan-García et al., for example, compared two stacking procedures and a sweeping method prior to a micellar electrokinetic chromatography (MEKC) separation for the analysis of a group of pesticides extracted from grapes and lettuces [5]. Hernández-Borges et al. [6,7] also tested several stacking techniques for the preconcentration of pesticides extracted from fruit juices [6] and soy milk [7] with success. Very recently, one of these techniques, reversed electrode polarity stacking mode (REPSM), was also used by Ravelo-Pérez et al. for the preconcentration of pesticides extracted from wines [8,9]. As a result, the application of on-line preconcentration schemes in the analysis of pesticides from real samples has not been fully explored.

Solid-phase microextraction (SPME) has only been applied in a relatively low number of occasions for the extraction of pesticides from fruit or vegetables [10–20]. Among these works,

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few have shown their analysis in tomato samples [12,14,16,20] and only Picó and co-workers [20] have used SPME for the extraction of a group of five pesticides from tomato extracts in combination with CE. In general, the number of works dealing with the analysis of pesticides by CE in fruits or vegetable samples is relatively low [2–4]. Therefore, the principal aim of this work is the development of a method for the simultaneous determination of a group of seven pesticides in tomatoes by the combined use of SPME with MEKC using REPSM as stacking technique to improve the limits of detection (LODs) of the method. To the best of our knowledge, this work represents the first determination of this group of pesticides in tomatoes by SPME-MEKC, also using an on-line preconcentration technique as REPSM.

2. Experimental

2.1. Samples and standard materials

All chemicals were of analytical reagent grade and used as received. Sodium dodecyl sulphate (SDS) and sodium tetraborate were from Sigma–Aldrich (Madrid, Spain). Sodium hydroxide and hydrochloric acid were from Merck (Darmstadt, Germany). Methanol and 1-propanol (HPLC-grade) were from Merck. Water was purified by using a Milli-Q system A10 (Millipore, Bedford, MA, USA). Pirimicarb, pyrimethanil, procymidone, nuarimol, fenarimol, benalaxyl and penconazole obtained from Sigma–Aldrich were used without further purification (purity >99.0%). Standard solutions of each pesticide were prepared in methanol (1 mg/ml) and kept in the dark under refrigeration at 4 °C. Tomato samples of different varieties were bought from local supermarkets (regional agricultural production).

2.2. REPSM-MEKC-diode array detection (DAD) conditions

MEKC-DAD analyses were performed in a PACE/5510 CE apparatus (Beckman, Fullerton, CA, USA) equipped with a DAD system working at 210 nm (except for pirimicarb which was 240 nm). System Gold Software was used for CE instrument control. Bare fused-silica capillaries with 50 μm i.d. were purchased from Composite Metal Services (Worcester, UK). The detection length was 50 cm and the total length was 57 cm. Injections were made at the anodic end using N_2 pressure. Before first use, fused-silica capillaries were rinsed (20 psi) with 2 min 1 M HCl, 2 min water, 5 min 0.1 M NaOH, 2 min water and 2 min running buffer. Capillary conditioning was done every morning by rinsing at 20 psi with water for 1 min and with background electrolyte (BGE) for 1 min. To achieve a good reproducibility between runs, the following washing protocol was applied (all using 20 psi): 1 min with methanol, 1 min with water and 1 min with BGE. At the end of the day, methanol was passed through the capillary for 1 min and water for 2 min. Electrophoretic separation was carried out at 25 °C and at +22 kV, using a BGE composed of 100 mM sodium tetraborate and 30 mM SDS at pH 8.5 plus 6% 1-propanol [21]. REPSM conditions were the following: the capillary is first filled with the BGE, then a large plug of sample is hydrodynamically injected for 11 s at 20 psi (1 psi = 6894.76 Pa), a high voltage (−22 kV) is then applied and the electric current is monitored to control sample matrix removal from the capillary; when the current becomes 95–99% of the value obtained with the BGE, the voltage is turned off and the polarity reversed to run the separation [21]. Analytes are dissolved in a 1:3 dissolution mixture made of water:100 mM sodium tetraborate at pH 8.5 (v/v).

2.3. SPME procedure

The SPME device for manual extraction, consisting in a holder assembly and several replaceable fibers was purchased from Supelco (Madrid, Spain) and used without modification. The fiber coatings used in this work were made of poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB, 60 μm). Before SPME extraction each fiber was conditioned in methanol with stirring for 30 min at 500 rpm and, between extractions, they were cleaned with water for 10 min and methanol for 20 min. Five grams of homogenized tomato were ultrasound-assisted extraction with 5 ml of acetone for 5 min. Extracts were evaporated to dryness at 45 °C using a rotavapor and reconstructed in 10 ml of Milli-Q water. This solution was later adjusted to pH 9.5 with 1 M NaOH and subjected to the SPME procedure. SPME extraction of the pesticides was carried out with the following procedure: 10.0 ml of the sample was placed into a 16.0 ml screw-cap vial containing a magnetic stirring bar and mixed with 3.0 g of NaCl (30% w/v). The fiber was immersed directly into the sample solution and the extraction took place at ambient temperature for 143 min with continuous stirring at 900 rpm. Then, desorption of the pesticides from the fiber was carried out with 1.0 ml of methanol by stirring for 13 min at 1000 rpm. The extract obtained from the SPME procedure was evaporated to dryness on a rotary evaporator at 40 °C and 250 mbar and reconstituted with 1.0 ml of the mixture 1:3 water:100 mM sodium tetraborate at pH 8.5 (v/v). Injection was carried out following the REPSM procedure (see Section 2.3). Tomato samples were fortified just after the homogenization of the whole vegetable and previous to the solvent extraction.

3. Results and discussion

The REPSM-MEKC separation of the group of pesticides selected in this work (see maximum residue levels (MRLs) in Table 1) was previously studied by our group for the analysis of these pesticides in water samples [21]. The method was found to be repeatable with acceptable sensitivity (LODs in the low μg/l range) and calibration data. Although the performance of the REPSM-MEKC method was already checked; in this work six consecutive injections of concentrations of the pesticides between 0.39 and 0.60 mg/l were carried out in the same day ($n = 6$) and on five consecutive days ($n = 30$). RSDs for peak areas and migration times are shown in Table 2.