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Analytical Methods

Application of magnetic solvent bar liquid-phase microextraction for determination of organophosphorus pesticides in fruit juice samples by gas chromatography mass spectrometry

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ABSTRACT

A simple, rapid and sensitive sample pretreatment technique, magnetic solvent bar liquid-phase microextraction (MSB-LPME) was developed for extracting organophosphorus pesticides from fruit juice. The analytes were extracted from the sample to the organic solvent immobilized in the fiber. The magnetic solvent bar not only can be used to stir the samples but also extract the analytes. After extraction, the analyte-adsorbed magnetic solvent bar can be readily isolated from the sample solution by a magnet, which could greatly simplify the operation and reduce the whole pretreatment time. The bar was eluted with methanol. The elute was evaporated to dryness and residue was dissolved in hexane. Several experimental parameters were investigated and optimized, including type of extraction solvent, number of magnetic solvent bar, extraction temperature, extraction time, salt concentration, stirring speed, pH and desorption conditions. The recoveries were in the range of 81.3–104.6%, and good reproducibilities were obtained with relative standard deviation below 6.1%.

1. Introduction

Organophosphorus pesticides (OPPs) are widely used in China for agricultural activities because of their high effectively and relatively low price (Jaleel, Gopi, Manivannan, & Panneerselvam, 2008; Xiong & Hu, 2008). However, the overuse of OPPs may lead to the contamination in agricultural products and, hence, in derivate food commodities, i.e., wine, fruit juices and so on (Albero, Sánchez-Brunete, & Tadeo, 2003; Liu, Hashi, Song, & Lin, 2005; Schellin, Hauser, & Popp, 2004; Wong, Webster, Halverson, Hengel, Ngim & Ebeler, 2003). The presence of OPP residues in foods become a health hazard to humans because some of them have a high acute toxicity due to the prevention of neural impulse transmission by their inhibition of cholinesterase (Barata, Porte & Solayan, 2004; Fu, Liu, Hu, Zhao, Wang & Wang, 2009; Sogorb & Vilanova, 2002; Vidair, 2004).

Fruit juice drinks are the favorite nutritional supplement. They are receiving considerable attention because they are comprised of highly abundant nutrition (e.g. vitamins and minerals) (Picó & Kozmutza, 2007). In addition, children are the largest group for the consumption of fruit juice products (Cortés-Aguado, Sánchez-Morito, Arrebola, Garrido Frenich, & Martínez Vidal, 2008). So pesticide residues may be transferred from fruit into juice, being a significant route to human exposure (Romero-González, Frenich & Vidal, 2008). The European Union Directive on drinking water quality (98/83/EC) established a maximum allowed concentration of 0.1 ng mL^{-1} for each individual pesticide and 0.5 ng mL^{-1} for total pesticides in drinking water. Although many regulators (e.g. European Union) have not set maximum residue limits for pesticides in fruit juices till now, it is also of great importance to develop rapid, highly sensitive, and easily operated methods to monitor pesticide residues in fruit juices.

A variety of analytical methods have been reported for the simultaneous determination of multiple pesticides in juice matrices. Liquid–liquid extraction (LLE) (Eva & Manuel, 2003; Kolbe & Andersson, 2006; Sannino, 2007) and solid phase extraction (SPE) (Albero, Sánchez-Brunete, & Tadeo, 2005; Topuz, Özhan & Alpertunga, 2005) are applied to the extraction of pesticides from juice samples. However, LLE is time-consuming and requires large volumes of organic toxic solvents. SPE uses much less solvent than LLE but the column needs pretreatment and

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can be relatively expensive and labor intensive. Nowadays, to overcome those problems, several microextraction techniques by reducing organic solvent consumption and simplifying the sample preparation techniques have been reported as alternatives to conventional sample preparation procedures, such as solid phase microextraction (SPME) (Cortés-Aguado et al., 2008; Simplício & Boas, 1999), stir bar sorptive extraction (SBSE) (Farajzadeh, Djozan, Nouri, Bamorowat, & Shalamzari, 2010; Zuin, Schellin, Montero, Yariwake, Augustod & Popp, 2006) and liquid-phase microextraction (LPME) (Lambropoulou & Albanis, 2007; Pintoa, Sontag, Bernardino, & Noronha, 2010). However, SPME and SBSE are time-consuming and the coated fibers or bars are generally expensive and easily destroyed. LPME is a solvent miniaturized procedure of LLE, which has a good preconcentration ability.

Hollow fiber liquid phase microextraction (HF-LPME) provides mechanical stability and protection to the organic solvent because the use of hollow fiber membrane, which is simple, effective, low cost, uses microliters of organic solvents and provides excellent sample clean-up ability, obtaining very clean extracts. Hollow fiber liquid phase microextraction (HF-LPME) is an LPME-based technique and has more advantages than LPME (Barahona, Gjelstad, Pedersen-Bjergaard &, Rasmussen, 2010; Bedendo, Jardim, & Carasek, 2012; Bolaños, Romero-González, Frenich, & Vidal, 2008). First, HF-LPME uses microliters of organic solvent which is placed in a hollow fiber, and then the analytes in the aqueous sample can be extracted into the organic solvent; second, the hollow fiber also plays a role as an excellent filter due to the large molecules cannot permeate through the pore in the hollow fiber; third, HF-LPME device is simple cost-efficient and easy operation. Thus, HF-LPME has attracts increasing attentions. So far, HF-LPME devices have highly flexible formats. The most common format is the hollow fiber fixed to a microsyringe during extraction so that the final extract may be withdrawn into the syringe and analyzed directly (Ouyang & Pawliszyn, 2006; Zhao, Zhu, & Lee, 2002; Zhu, Zhu, & Lee, 2001). Pedersen-Bjergaard and Rasmussen (1999) first reported the U-shaped HF-LPME (Pedersen-Bjergaard & Rasmussen, 1999). Jiang and Lee (2004) proposed solvent bar microextraction (SBME). The organic extracting solvent (1-octanol) was confined within the hollow fiber membrane (sealed at both ends) that was placed in a stirred aqueous sample solution. Due to the free movement of the solvent bar in the sample solution, rapid extraction equilibrium can be achieved. Hultgren, Larsson, Nilsson, and Jönsson (2009) fixed the fiber on a 4 cm metal rod from it end for keeping it at a fixed position in the stirring sample. Yu et al. proposed dual solvent-stir bars microextraction (DSSBME), a stainless-steel wire was used to fix the hollow fibers and the device could stir by itself (Yu, Liu, Lan, & Hu, 2008). Although the devices of HF-LPME are developed rapidly, few of devices can be used as both the stirring bar of microextraction, and extractor of the analytes.

This paper aims to present a new extraction alternative that provides a simple and easy method to extract analytes from the complex matrices. A magnetic solvent bar liquid-phase microextraction (MSB-LPME) was first applied for the extraction of OPPs in juice samples. The MSB-LPME devices cheaply manufactured and easily assembled. The stainless-steel wire was inserted into the hollow of the hollow fiber, and the stainless-steel wire not only used as the magnet stirrer, but also achieved magnetic separation which was isolated from the sample matrix easily with an external magnetic field. The operation for the sample treatment was simple and the problem of solvent bar floating up on the samples was solved. Several experimental conditions were studied and optimized. The performances of developed method were evaluated.

2. Experimental

2.1. Chemicals and reagents

Eight OPPs including phorate, diazinon, tebupirimfos, tolclofos-methyl, pirimiphos-methyl, fenthion, fenamiphos, and sulprofos were purchased from National Institute of Metrology (Beijing China), and the purity of OPPs is ⩾98%. Stock solutions for the OPPs were prepared in acetone at 1000 μg mL^{-1} and stored at 4 °C. Working standard solutions were prepared daily by diluting the stock solution with acetone. Analytical reagent grade ethyl acetate, chloroform, hexane, 1-octanol and toluene were obtained from Beijing Chemical Factory (Beijing, China). Pure water was obtained with a Milli-Q water system (Millipore, Billerica, MA, USA).

Q3/2 Accurel PP hydrophobic polypropylene hollow fiber membrane (600 μm inner diameter, 200 μm wall thickness and 0.2 μm pore size) was purchased from Membrana GmbH (Wuppertal, Germany). The stainless-steel wire (505 μm outer diameter) was just fit the hollow fiber membrane.

2.2. Instruments and apparatus

The analytical solution was analyzed using GC–MS QP 2010 (Shimadzu, Kyoto, Japan). Chromatographic separation was conducted with a DB-5MS capillary column (30 m × 0.25 mm I.D., film thickness of 0.25 μm, J & W Scientific, Folsom, CA, USA). Helium (purity ⩾ 99.999%) was used as carrier gas at a constant flow of 1.0 mL min^{-1}. The temperature program was set initially at 70 °C for 3 min; ramp to 170 °C at a rate of 15 °C min^{-1}, held for 9 min; and then ramp to 200 °C at a rate of 3 °C min^{-1}, held for 1 min; finally raised to 230 °C at a rate of 10 °C min^{-1}, held for 2 min. Injector temperature was maintained at 280 °C, and the injection volume was 1.0 μL in a 5:1 split ratio. Mass spectrometric parameters: electron impact ionization mode with an ionizing energy of 70 eV, injector temperature 280 °C interface temperatures 250 °C, ion source temperature 200 °C. The mass spectrometer was operated in the selected ion monitoring (SIM) mode for quantitative analysis and the characteristic ions are given in Table 1. Full-scan MS data were acquired in the range of m/z 50–900 to obtain the fragmentation spectra of the analytes.

2.3. Sample preparation

The fruit juice samples, including lemon juice, apple juice, peach juice and orange juice were purchased from local supermarket (Changchun, China). The fresh spiked samples containing OPPs were prepared by spiking the mixed working standard solutions into juice samples and shaking for 10 min. Except for the experiments mentioned in Section 3.2.3, which were performed with all four samples, all other experiments were performed with lemon juice sample. All experiments were performed in triplicate.

2.4. MSB-LPME procedure

The magnetic solvent bar (MSB) was designed (Fig. 1(A)), and it contained the hollow fiber and stainless-steel wire. The hollow fiber and stainless-steel wire were both manually and carefully cut into segments of 1.2 cm length. These segments were ultrasonically cleaned in an ultrasonic bath to remove impurities, and dried in the air. In order to prepare the extraction unit, the stainless steel wire was inserted into the hollow of the hollow fiber. Then the resulting fiber piece was immersed in 1-octanol for 1 min in order to impregnate pores of the fiber wall. In order to remove the extra