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An efficient, rapid and microwave-accelerated dispersive liquid–liquid microextraction method for extraction and pre-concentration of some organophosphorus pesticide residues from aqueous samples

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ABSTRACT

In this paper, microwave-accelerated dispersive liquid–liquid microextraction has been developed for the extraction/preconcentration of some organophosphorus pesticides from aqueous samples prior to their analysis by gas chromatography–flame ionization detection. In this method, temperature of a high volume of aqueous sample is elevated by a microwave oven and then a mixture of extraction and disperser solvents is rapidly injected into the aqueous phase. After cooling to room temperature, the phase separation is accelerated by centrifuging. The main experimental factors affecting performance of the method including type and volume of the extraction and disperser solvents, temperature, pH, and salt addition were investigated and optimized. Under the optimum extraction conditions, the method resulted in low limits of detection and quantification within the ranges of 0.65–1.3 and 2.2–4.5 $\mu g\,L^{-1}$, respectively. Relative standard deviations were in the range of 2–7% ($C = 40$ or 100 $\mu g\,L^{-1}$) for intra-day ($n = 6$) and inter-day ($n = 4$) precisions. Finally, the proposed method was successfully applied to analysis of the target analytes in surface water and well water and fruit juice samples; diazinon was determined at $\mu g\,L^{-1}$ level in apple juice.

1. Introduction

The presence of organophosphorus (OPP) residues in foods is a health hazard because some of them have a high acute toxicity to humans, due to the prevention of neural impulse transmission by their inhibition of cholinesterase (Barata et al., 2004; Fu et al., 2009; Sogorb and Vilanova, 2002; Vidair, 2004). 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. Chromatographic methods, such as gas chromatography (GC) and high-performance liquid chromatography (HPLC) coupled with various detection systems are powerful tools for the analysis of OPP residues in samples such as environmental water (Nedaei et al., 2014; Wang et al., 2011a,b), fruits (Sharma et al., 2010; Wang et al., 2013), and fruit juices (Patel et al., 2006).

Traditionally, the extraction and pre-concentration of analytes from sample matrices are often accomplished by procedures such as liquid–liquid extraction (LLE) (Sannino, 2007) and solid-phase extraction (SPE) (Albero et al., 2005; Fang et al., 2012). Recently, much attention is being paid to development of miniaturized, more efficient and environmentally friendly extraction methods which could greatly reduce the consumption of organic solvents.

In liquid-phase microextraction (LPME) (Liu and Dasgupta, 1996) analytes are normally extracted into a small amount of a water-immiscible solvent (acceptor phase) from an aqueous sample containing the analytes (donor phase) (Barahona et al., 2010; Pinto et al., 2010; Wu et al., 2015). LPME can be divided into three main categories, including single-drop microextraction (SDME), hollow fibre liquid-phase microextraction (HF–LPME), and dispersive liquid–liquid microextraction (DLLME). SDME consists of the suspension of a drop by a microsyringe into an

Abbreviations: EF, enrichment factor; ER, extraction recovery; FID, flame ionization detector; GC, gas chromatography; LLE, liquid–liquid extraction; LOD, limit of detection; LOQ, limit of quantification; LPME, liquid phase microextraction; LR, linear range; MS, Mass spectrometry; RSD, relative standard deviation; SDME, single–drop microextraction; SPE, solid phase extraction; SPME, solid phase microextraction; MWA–DLLME, microwave–accelerated dispersive liquid–liquid microextraction.

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aqueous solution (Jeannot and Cantwell, 1997; Liang et al., 2008; Xu et al., 2007). The drawbacks of SDME have been partially overcome by applying hollow fibre (Psillakis and Kalogerakis, 2003; Rasmussen and Pedersen-Bjergaard, 2004). In HF–LPME method, the hollow fibre is used for clean-up of sample matrix along with the extraction of analytes. However, this method is limited by the small contact surface area of the fibre, which necessitates a long extraction time. To overcome this disadvantage, Assadi and co-workers developed a novel LPME technique termed DLLME (Rezaee et al., 2006), which is based on a ternary component solvent system. The advantages of DLLME method are simplicity of operation, rapidity, low cost, high extraction recovery (ER), high enrichment factor (EF), and decreasing waste generation (Cunha et al., 2009; Farajzadeh et al., 2011).

The aim of this study was to develop microwave–accelerated DLLME (MWA–DLLME) in which high volume of aqueous phase is used to reach very high EFs in the extraction and pre-concentration of some OPP residues prior to their analysis by gas chromatography–flame ionization detection (GC–FID). Up to now microwaves have been used for accelerating digestion of solid samples or extraction of the analytes from solid or semi-solid samples. However in this study firstly the samples used are liquid and secondly microwaves are used in accelerating a micro-extraction technique, e.g., DLLME. In this method, the temperature of the aqueous sample is rapidly elevated in a microwave oven and then a mixture of extraction and disperser solvents is injected into the aqueous sample at the elevated temperature. Several important parameters affecting the efficiency of the method, such as the type and volume of extraction and disperser solvents, temperature, pH, and ionic strength of the sample solution were carefully studied. The proposed method was successfully applied to the determination of selected OPPs in fruit juices and environmental water samples.

2. Experimental

2.1. Reagents and solutions

The OPPs used (diazinon, malathion, and chlorpyrifos) with purity >98% were kindly provided by GYAH Corporation (Karadj, Iran). Organic solvents were from the following sources: 1,2-dibromoethane (1,2-DBE), 1,1,2-trichloroethane (1,1,2-TCE), dimethylformamide (DMF), dimethylsulfoxide (DMSO), 1,4-dioxane, and *n*-propanol from Merck (Darmstadt, Germany); and 1,1,2,2-tetrachloroethane (1,1,2,2-TCE) from Janssen (Beerse, Belgium). Analytical-reagent grade sodium chloride, hydrochloric acid, and sodium hydroxide were also obtained from Merck. Deionized water was obtained from Ghazi Company (Tabriz, Iran). A stock solution of OPPs (1000 mg L^{-1} of each OPP) was prepared by dissolving an appropriate amount of each pesticide in acetone. Working standard solutions were prepared daily by diluting the stock solution with deionized water. A mixture standard solution of the analytes (125 mg L^{-1} of each OPP) in 1,2-DBE (extraction solvent) was prepared and directly injected into the separation system each day (three times), in order to evaluate the instrumental system quality and to calculate EFs and ERs.

2.2. Samples

Apple, grape, and sour cherry juices with different brands were obtained from local supermarkets (Tabriz, Iran). Surface water and well water were collected from a garden (Ardabil, Iran). The apple and grape juice samples were diluted at a ratio of 1:2 with deionized water and then used. The sour cherry juice was diluted with deionized water at a ratio of 1:3. Well water and surface water were used without dilution.

2.3. Instrumentation

A gas chromatograph (GC-2014; Shimadzu, Kyoto, Japan) equipped with a split/splitless injector and an FID was used for the separation and determination of the selected OPPs. Helium (99.999%, Gulf Cryo, United Arabic Emirates) was used as the carrier gas at a fixed linear velocity of 30 cm s^{-1} and make up gas (at a flow rate of 30 mL min^{-1}). Chromatographic separation was achieved on an RTX-1 (100% dimethylpolysiloxane) capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm) (Restek, Bellefonte, PA). The column oven temperature was initially held at 40 °C for 2 min, then raised to 250 °C at a rate of 10 °C min^{-1}, and was held at 250 °C for 4 min. The FID temperature was maintained at 250 °C. Hydrogen gas was generated with a hydrogen generator (OPGU-1500S; Shimadzu) for the FID at a flow rate of 40 mL min^{-1}. The flow rate of air was 300 mL min^{-1}.

The pH measurements were performed with a Metrohm pH meter model 654 (Herisau, Switzerland). A Hettich centrifuge (Model ROTOFIX 32 A; Tuttlingen, Germany) was used for accelerating phase separation. A microwave oven model NN-S 235 WF (Panasonic, Fujisawa, Japan) was used for heating the aqueous phase. Gas chromatography–mass spectrometry (GC–MS) analysis was carried out on an Agilent 7890A-5975C instrument (Agilent Technologies, Santa Clara, CA). The MS operational conditions were: ion source, electron impact (EI) at 70 eV; ionic source temperature, 250 °C; transfer line temperature, 260 °C; mass range, *m*/*z* 55–350; acquisition rate, 20 Hz; and detector voltage, −1700 V. Library searching was performed using the commercial NIST library. The carrier gas was helium at a flow rate of 1.0 mL min^{-1}. The capillary column and column oven temperature programming were the same as used in GC–FID analysis mentioned above.

2.4. Procedure

A 50-mL sample or standard solution of the analytes with a concentration of 1 mg L^{-1} of each pesticide was transferred into a 70-mL glass test tube with conical bottom. Afterward, temperature of solution was elevated to 80 °C by the microwave oven (33 s, high power, and frequency 2450 MHz). Then, a mixture of 150 μL of the extraction solvent (1,2-DBE) and 1.5 mL of the disperser solvent (DMSO) were rapidly injected into the solution using a 5-mL glass syringe. Consequently, 1,2-DBE was dispersed completely in all parts of the aqueous solution without any need for agitation, leading to a partially turbid solution. The solution was cooled with tap water for 5 min. During this action, turbidity of the solution increased intensively. Then, the solution was centrifuged at a rate of 1400 g for 8 min. During this process, 25 ± 2 μL of 1,2-DBE settled at the bottom of the tube. Finally, 1 μL of the 1,2-DBE phase was injected into the GC system for analysis.

2.5. Calculation of EFs and ERs

In order to obtain the optimized extraction conditions, EFs and ERs were used to evaluate the extraction efficiency under different conditions. EF is defined as a ratio of the analyte concentration in the sedimented phase (C_{sed}) to the initial concentration of the analyte (C_0) within the sample:

$$EF = \frac{C_{sed}}{C_0} \quad (1)$$

C_{sed} was obtained from the comparison of the analytes peak areas in two cases: direct injection of the standard solution (1000 mg L^{-1} of each analyte) prepared in 1,2-DBE and injection of the sedimented phase after performing the proposed method.