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Analytical Methods

Application of elevated temperature-dispersive liquid-liquid microextraction for determination of organophosphorus pesticides residues in aqueous samples followed by gas chromatography-flame ionization detection

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ABSTRACT

In the present study, an elevated temperature, dispersive, liquid-liquid microextraction/gas chromatography-flame ionization detection was investigated for the determination, pre-concentration, and extraction of six organophosphorus pesticides (malathion, phosalone, dichlorvos, diazinon, profenofos, and chlorpyrifos) residues in fruit juice and aqueous samples. A mixture of 1,2-dibromoethane (extraction solvent) and dimethyl sulfoxide (disperser solvent) was injected rapidly into the sample solution heated at an elevated temperature. Analytical parameters, including enrichment factors (1600–2075), linearity ($r > 0.994$), limits of detection (0.82–2.72 ng mL^{-1}) and quantification (2.60–7.36 ng mL^{-1}), relative standard deviations (<7%) and extraction recoveries (64–83%), showed the high efficiency of the method developed for analysis of the target analytes. The proposed procedure was used effectively to analyse selected analytes in river water and fruit juice, and diazinon was found at ng mL^{-1} concentrations in apple juice.

1. Introduction

Organophosphorus pesticides (OPPs) are applied extensively throughout the world due to their wide activity against pests and relatively low cost. They are also gradually replacing organochlorine pesticides due to their low environmental persistence (You, Xing, Liu, & Jiang, 2013; Lin, Huang, & Liu, 2006). Generally, OPPs are used for different classes of vegetables, grain crops and fruits (Jalali, Balali-Mood, Jalali, & Shakeri, 2012) to enhance quality and yield. Frequently, pesticides are used during the growth period and, sometimes, at the fruiting phase. OPPs are an important source of environmental contamination due to their widespread use (Padrón-Sanz et al., 2005; Tsoukali, Theodoridis, Raikos, & Grigoratou, 2005) and contaminate agricultural products, such as fruit juices.

OPPs penetrate the crop matrices and are converted to compounds that are toxic for human (Yao, Jiang, Liu, & Cheng, 2001). Neurological symptoms are the most reported effects of OPPs toxicity. For example, OPPs inhibit the acetyl-cholinesterase function in the transmission of nerve-impulse (Maroni, Colosio, Ferioli, & Fait, 2000). Other effects have not been well studied, but are

Abbreviations: EF, enrichment factor; ET-DLLME, elevated temperature-dispersive liquid-liquid microextraction; FID, flame ionization detection; GC, gas chromatography; LR, linear range; LOQ, limit of quantification; LOD, limit of detection; MS, mass spectrometry.

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important in risk assessment. European Union regulations have defined maximum residue limits (MRLs) for OPPs in food and water samples in the range 0.01–0.5 mg kg^{-1} and 20–100 μg L^{-1}, respectively [http://ec.europa.eu/sanco-pesticides/public/event=homepage]. Thus, development of a simple, rapid, sensitive method to detect the residues of pesticides in foods is important.

Several analytical methods have been developed for the determination of OPPs in aqueous samples, such as high-performance liquid chromatography (HPLC) (Farajzadeh, Bahram, Vardast, & Bamorowat, 2011), capillary electrophoresis (CE) (Li, Zhou, Jin, Zhang, & Liu, 2010), and gas chromatography (GC) (Bidari, Ganjali, Norouzi, Hosseini, & Assadi, 2011). However, to concentrate and isolate the compounds of interest, sample preparation step is generally required. Traditionally, extraction and enrichment of analytes are usually done by solid phase extraction (SPE) (Wang & Du, 2010; De la Colina, Peña Heras, Dios Cannela, & Sánchez Rasero, 1993) or liquid-liquid extraction (LLE) (Borges, Freire, Martins, & Siqueira, 2009; Park, Pyo, Park, & Park, 2005). But, these techniques often require large sample volumes and use organic solvents as well as being time-consuming, which make them costly, difficult and tedious. In the recent years, economic, efficient miniaturized sample preparation methods have been developed, such as solid phase microextraction (SPME) (Alpendurada, 2000; Penalver, Pocurull, Borrull, & Marce, 1999) and liquid phase microextraction (LPME) (Psillakis & Kalogerakis, 2003; Rasmussen & Pedersen-Bjergaard, 2004). LPME is a miniaturized sample preparation method in which a few microliters of an organic solvent are used as a solvent (Liu & Dasgupta, 1995). Rezaee et al. (2006) developed a LPME method, specifically dispersive liquid-liquid microextraction (DLLME). In this method, a mixture of disperser and extraction solvents quickly disperses in an aqueous sample forming a cloudy solution. The cloudy solution indicates dispersion of the solvents in an aqueous solution with a large surface contact area. The analytes are extracted and enriched in the fine droplets of solvent, which are then separated by centrifugation (Rahnama Kozani, Assadi, Shemirani, Millani Hosseini, & Jamali, 2007). Lately, a new version of DLLME, namely elevated temperature-dispersive liquid-liquid microextraction (ET-DLLME), has been proposed (Farajzadeh, Afshar Mogaddam, & Gorbanpour, 2014). The difference with this method from traditional DLLME is the use of a pre-heated sample that disperses immediately on injection into the solvents. At a high temperature, solubility of the solvent in an aqueous solution is higher compared with an ambient or low temperature sample. After injection, the solution cools and forms more droplets of the extraction solvent leading to greater extraction efficiency.

The main goal of this study was application of the ET-DLLME method followed by GC determination for some OPP residues in an aqueous sample. Using a high volume of sample (50 mL) and a low volume of the disperser solvent (1.5 mL *vs.* 50 mL sample solution), high enrichment factors could be achieved. In addition, a relatively small volume of the extraction solvent was used (μL level *vs.* 50 mL sample solution). Different experimental conditions affecting the microextraction efficiency were examined and the selected pesticides (common pesticides used in Iran) determined in water and fruit juice samples.

2. Material and methods

2.1. Materials and reagents

All OPPs (dichlorvos, diazinon, malathion, chlorpyrifos, profenofos, and phosalone) with purities >98% were obtained from GYAH Corporation (Karaj, Iran). 1,1,2-Trichloroethane (1,1,2-TCE) (98%) and 1,1,2,2-tetrachloroethane (1,1,2,2-TCE) (97%) were from Janssen Chimica (Beerse, Belgium). 1,2-Dibromoethane (1,2-DBE) (>98%) was from Merck (Darmstadt, Germany). The tested disperser solvents, including HPLC-grade dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), and *n*-propanol and compounds such as sodium hydroxide, hydrochloric acid, and sodium chloride, were also obtained from Merck. Deionized water (Ghazi Company, Tabriz, Iran) was used for the preparation of aqueous solutions. Stock solutions of the OPPs at 1000 mg L^{-1} (each analyte) was prepared by dissolving appropriate amounts in acetone. The stock solution was diluted to obtain working solutions using deionized water. For system control, and calculation of enrichment factors and extraction recoveries, a standard solution was prepared in 1,2-DBE at 150 mg L^{-1} for each pesticide. This solution was injected directly into the system three times a day.

2.2. Instruments

A Shimadzu gas chromatograph GC-2014 (Shimadzu, Kyoto, Japan), equipped with a split/splitless injector adjusted at 300 °C in a splitless mode (sampling time 1 min) and a flame ionization detector (FID), was used in this study. Helium (Gulf Cryo, United Arab Emirates – purity of 99.999%) was used as the carrier gas at a constant linear velocity (30 cm s^{-1}). An OPTIMA delta-3 capillary column (30 m × 0.25 mm i.d., and the film thickness of 0.5 μm) (Macherey-Nagel, Germany) was used for separation of the target OPPs. Hydrogen was produced using a hydrogen generator (OPGU-1500S, Shimadzu, Japan) and FID was at a flow rate of 30 mL min^{-1}. The column oven was programmed as follows: initially held at 50 °C for 1 min, then the temperature was raised to 300 °C at a rate of 15 °C min^{-1}, and held at 300 °C for 2 min. The FID temperature was adjusted at 300 °C. An Agilent 7890A gas chromatograph equipped with a 5975C mass selective detector (Agilent Technologies, CA, USA) was used in gas chromatography–mass spectrometry (GC–MS) analysis. The system was equipped with a split/splitless injector operated at 300 °C in a splitless mode (sampling time 1 min). An HP-5 MS capillary column (30 m × 0.25 mm i.d., and the film thickness of 0.25 μm) (Hewlett-Packard, Santa Clara, USA) was used for separation of the OPPs in the GC–MS system. In the GC–MS and GC-FID systems, the oven temperature programmes were the same. The MS operational conditions were: ionic source temperature: 250 °C, electron ionization (EI) at 70 eV; mass analyzer: quadruple; mass range: *m/z* 55–350; transfer line temperature: 260 °C; acquisition rate: 20 Hz; and detector voltage: −1700 V. The commercial NIST library was used to confirm identify. A Metrohm pH meter model 654 (Herisau, Switzerland) was used to monitor pH. A ROTOFIX 32A centrifuge (Hettich, Germany) was also used throughout.

2.3. Samples for analysis

Samples, such as onion, and grape and apple juices were purchased from local vendors (Tabriz, Iran). The onions were cut into small pieces and 100 g was squeezed using a commercial food processor (Black & Decker, USA). The onion juice was diluted with deionized water at a ratio of 1:10. Two river water samples were collected from the Zarrineh and Simineh rivers (Miandoab, West Azarbaijan, Iran). The river waters were used without filtration or dilution. The apple and grape juice samples were diluted with deionized water at a ratio of 1:2 before analysis. All samples were stored in a refrigerator at 4 °C before analysis.

2.4. Sample preparation method

A 50 mL of each sample or standard solution containing NaCl (5%, *w/v*) was transferred into a 70-mL conical bottom glass test tube. The tube was placed in a water bath (at 80 °C) for 5 min