



ORIGINAL ARTICLE

Miniaturized counter current liquid–liquid extraction for organophosphorus pesticides determination



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Abstract In the present work, a simple, rapid, sensitive and economical sample pre-treatment technique; miniaturized counter current liquid–liquid extraction was developed for the determination of organophosphorus pesticide (OPP) residue in water samples and compared with conventional dispersive liquid–liquid microextraction. Gas chromatography–flame ionization detector (GC/FID) was used for OPP quantification. Two OPPs (diazinon and malathion) were selected as model compounds and the proposed methods were carried out for their preconcentration from water samples. The presented method was based on dispersive liquid–liquid extraction with methanol containing butyl acetate as a solvent with density lower than water. After phase separation, butyl acetate was injected into the GC/FID instrument. The linearity was obtained in the concentration range of 0.4–1000.0 $\mu\text{g L}^{-1}$ and correlation coefficients were in the range of 0.999–0.997 for diazinon and malathion, respectively. The limits of detection (LODs), was based on signal-to-noise ratio (S/N) of 0.1 $\mu\text{g L}^{-1}$ for two pesticides.

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Introduction

Water contamination due to the wide variety of pesticides used in agriculture is a global environmental pollution problem.

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Organophosphorus pesticides (OPPs) are widely found in water resources. They are released into the environment from manufacturing, transportation, and agricultural applications (Farajzadeh et al., 2009). In environmental samples the analyte is often present in only trace concentrations and the matrix is complicated. In order to reach at sub- $\mu\text{g L}^{-1}$ levels of detection, an efficient extraction and preconcentration technique is required (Zhao et al., 2007). Traditional solvent extraction has been used for many years as the basic, powerful method of concentration. However, it requires large amounts of organic solvents and nowadays attention is focused on techniques that are environmentally friendly and reduce the cost of analysis by reduction or complete elimination of organic solvents (Ojeda and Rojas, 2009; Sarafraz-Yazdi and Amiri, 2010). In

recent years, the development of fast, precise, accurate and sensitive methodologies has become an important issue. Liquid phase microextraction (LPME) has been developed as a mini-mized-solvent-based pretreatment method. (Pusvaskiene et al., 2009; Moinfar and Milani Hosseini, 2009). Homogeneous liquid–liquid extraction (HLL) and dispersive liquid–liquid microextraction (DLLME) are novel environmentally benign sample-preparation techniques, possessing obvious advantages of simple operation with a high enrichment factor, low cost, and low consumption of organic solvent (Kocurova et al., 2012). In DLLME, the appropriate mixture of extraction and disperser solvents is rapidly injected by a syringe into an aqueous sample containing the analytes of interest. DLLME employs a mixture of a high-density solvent (extractant) and a water miscible, polar solvent (disperser). Acetone, methanol and acetonitrile can be used as dispersers, whereas chlorinated solvents such as chlorobenzene, carbon tetrachloride and tetrachloroethylene are useful as extractants. Other non chlorinated solvents such as undecanol, 1-dodecanol, 2-dodecanol and n-hexadecane can also be used. In practice, a cloudy solution forms, resulting from the formation of fine droplets of the extraction solvent, which disperse in the sample solution and after centrifuging, the fine droplets settle at the bottom of the conical test tube. Sample preparation plays an important role in the field of pesticide residue analysis. In all HLL and DLLME methods, analyte was extracted from the aqueous phase, but our team introduced a novel miniaturized HLL for extraction of polycyclic aromatic hydrocarbons and pesticides from the methanolic phase by *n*-hexane as a solvent of lower density than water (Hassan et al., 2010; Shamsipur and Hassan, 2010) called low density miniaturized homogenous liquid–liquid extraction (LDMHLL). The development of miniaturized methodologies that combines high throughput analysis, low cost, and environmental sustainability, is of great current concern. The aim of this study was to develop a new version of our previous method that we can call it as miniaturized counter current liquid–liquid extraction (MCCLLE) (in this method sample phase and extracting solvent move against each other) for determination of OPPs by GC/FID.

Experimental

Reagents and materials

All chemicals were of reagent grade and were used without further purification. Analytical grade methanol, chloroform, butyl acetate, toluene, benzene, diethyl ether and methyl-*t*-butyl ether and sodium chloride were purchased from Merck (Darmstadt, Germany). Diazinon, malathion and chlorpyrifos were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Stock solution of pesticides was prepared at a concentration of 1000.0 mg L⁻¹ in methanol. The working solutions were prepared at an appropriate concentration from stock solutions and stored at -20 °C. Intermediate stock solution of pesticide was prepared at a concentration of 100.0 mg L⁻¹ in methanol and stored in a refrigerator (4 °C) until use. The working solution was prepared by an appropriate dilution of the stock solution with the methanol. Chlorpyrifos was prepared at 50.0 mg L⁻¹ in extraction solvent and used as internal standard. Purged water was prepared on a Direct-Q 3 UV with a pump system (Millipore, Molsheim, France).

Apparatus

The extracted compounds were analyzed on a 7890 A agilent gas chromatograph coupled to flame ionization detector (Agilent Technologies, Avondale, PA, USA) and 2 μL of the sample was injected into the splitless mode at 250 °C into a 30 m × 0.25 mm × 0.25 μm DB-5 MS capillary column and operated by Chemstation Software (Agilent Technologies). The temperature program used for the chromatographic separation is as follows: 50 °C for 2 min, temperature increase at 25 °C min⁻¹ to 100 °C and held for 2 min, and then temperature increase at 20 °C min⁻¹ to 270 °C where it was finally held for 4 min. The carrier gas was helium (99.999%) and was kept at a constant flux of 1.0 mL min⁻¹. The FID temperature was maintained at 290 °C and hydrogen gas was generated by a hydrogen generator (Dominick Hunter, United Kingdom) for FID at a flow rate of 30 mL min⁻¹. The flow rate of zero air (99.999%, Air Products, UK) for FID was 400 mL min⁻¹.

Counter current liquid–liquid extraction procedure

500.0 μL of methanol containing 100.0 μL of butyl acetate was placed in a 10 mL dry narrow neck volumetric flask. By adding 10.0 mL of aqueous sample into volumetric flask, butyl acetate was separated at the top of volumetric flask and was drawn out by a Hamilton syringe and transferred to a conical vial and 2.0 μL of butyl acetate was injected into GC/FID for quantitative analysis.

Dispersive liquid–liquid microextraction procedure

For the DLLME, a 10.00-mL aliquot of aqueous sample was placed in a 10-mL screw-cap glass tube with conical bottom. 500.0 μL of methanol containing 100.0 μL CHCl₃ was injected rapidly into the sample solution by 1.00-mL syringe and then the solution is vortexed for 5 s. A cloudy solution which consisted of very fine droplets of CHCl₃ that dispersed into aqueous sample was formed, and the analytes were extracted into the fine droplets. After centrifugation at 3500 rpm for 5 min, the CHCl₃ phase was sedimented at the bottom of the centrifuge tube. The sedimented phase was completely transferred to another test tube with conical bottom using 100 μL syringe and 2.0 μL of the CHCl₃ phase injected into the GC system for analysis.

Results and discussion

The theory of DLLME and MCCLLE is similar to that of LLE. Thus, the equations that describe the effects of several parameters on the efficiency of the proposed method are similar to those of LLE. The partition coefficient (*K*) is defined as the ratio of the analyte concentration in the extracting phase (*C*_{eq}^{ex}) and the final concentration of the analyte in the source sample solution (*C*_{eq}^{sam}):

$$K = \frac{C_{eq}^{ex}}{C_{eq}^{sam}} \quad (1)$$

$$E_r = \frac{n_{ex}}{n_{ini}} = \frac{C_{eq}^{ex} V_{ex}}{C_{ini}^{sam} V_{sam}} \quad (2)$$

$$P_f = \frac{C_{eq}^{ex}}{C_{ini}^{sam}} \quad (3)$$

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