Food Chemistry 192 (2016) 596–602

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Dynamic microwave-assisted extraction combined with continuous-flow microextraction for determination of pesticides in vegetables

Lijie Wu [a], Mingzhu Hu [a], Zhanchao Li [a], Ying Song [a], Cui Yu [b], Hanqi Zhang [a], Aimin Yu [a], Qiang Ma [c], Ziming Wang [a,*]

[a] College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China
[b] School of Chemical and Materials Engineering, Yanching Institute of Technology, Langfang 065201, China
[c] Chinese Academy of Inspection and Quarantine, Beijing 100123, China

ARTICLE INFO

Article history:
Received 3 March 2015
Received in revised form 9 July 2015
Accepted 12 July 2015
Available online 14 July 2015

Keywords:
Dynamic microwave-assisted extraction
Continuous-flow microextraction
Organophosphorus pesticides
Fresh vegetables
Gas chromatography mass spectrometry

ABSTRACT

A simple, rapid, solventless and cost-effective dynamic microwave-assisted extraction (DMAE) combined with continuous-flow microextraction (CFME) system was firstly assembled and validated for extraction of eight organophosphorus pesticides in vegetables. The method combines the advantages of DMAE and CFME, and extends the application of the single drop microextraction to complex solid samples. The extraction, separation, and enrichment were performed in a single step, which could greatly simplify the operation and reduce the whole pretreatment time. In the developed method, analytes were first extracted from the vegetables using 3% NaCl solution as extraction solvent, then concentrated into microextraction solvent. After extraction, the microextraction solvent containing the enriched analyte was directly analyzed by GC–MS without any filtration or clean-up process. Several parameters affecting the extraction efficiency were investigated and optimized. Real vegetable samples were analyzed, satisfactory recoveries were obtained in the range of 80.7–106.7%, and relative standard deviations were lower than 8.7%.

1. Introduction

Organophosphorus pesticides (OPPs) are widely used in agriculture around the world to control pests, weeds, diseases and to increase harvest productivity (Ho, Tsoi, & Leung, 2013; Rissato, Galhiane, Apon, & Arruda, 2005). But the overuse of OPPs involves the risk of their retention in crops. It is well known that OPPs have high toxicity due to the prevention of neural impulse transmission by their inhibition of cholinesterase, which can cause risk to human health and life (Fu et al., 2009; Sogorb & Vilanova, 2002). Considering the public health and food safety, a simple, rapid and sensitive analytical method for determination of OPPs in foods and environmental matrices is required.

The low concentration of OPPs and the complex matrix of many samples make sample preparation necessary for the reliable determination of these compounds. The sample preparation step typically consists of extraction to isolate and enrich the components of interest from a sample matrix in an analytical process (Rezaee et al., 2006). More recently, an interesting alternative to conventional LLE is liquid phase microextraction (LPME) based on the use of smaller amounts of organic solvent and a large amount of aqueous solvent (Psillakis & Kalogerakis, 2002, 2003), which was introduced by Liu and Dasgupta in 1996 (Liu & Dasgupta, 1996). Different approaches have been developed for LPME, such as single drop microextraction (SDME) (Jeannot & Cantwell, 1996, 1997), hollow fiber–liquid phase microextraction (HF–LPME) (Pedersen-Bjergaard & Rasmussen, 1999), dispersive liquid–liquid microextraction (DLLME) (Zhou, Bai, Xie, & Xiao, 2008), solidification of floating organic drop microextraction (Khalili Zanjani, Yamini, Shariati, & Jönsson, 2007) and continuous flow microextraction (CFME) (Liu & Lee, 2000).

In CFME method, the extraction solvent drop is injected into a glass chamber using a conventional microsyringe and held at the outlet tip of a PTFE connection tube; the solvent drop interacts continuously with the sample solution and extraction proceeds simultaneously with the help of a HPLC pump; the organic drop was collected by a microsyringe after extraction and directly injected to GC for analysis. So this method can gain higher concentration factor and extraction speed (Sarafraz-Yazdi & Amiri, 2010)

* Corresponding author.
E-mail address: wangziming@jlu.edu.cn (Z. Wang).

http://dx.doi.org/10.1016/j.foodchem.2015.07.055
0308-8146/

and has been successfully used for determination phthalate esters (Liang, Li, Xu, & Du, 2008), pesticides (Guo, Liang, Zhang, Liu, & Liu, 2005; He & Lee, 2006; Liu, Chen, Yang, & Wang, 2007), aromatic amines (Liu, Hashi, & Lin, 2007), and some trace elements (Cao, Liang, & Liu, 2008; Xia, Hu, Jiang, Wu, & Liang, 2004) in water samples. However, up to the present, there was no report about application of CFME in the extraction of trace analytes in complex solid matrixes.

Microwave-assisted extraction (MAE) has been proved to be a versatile extraction technique with the advantages of rapidity, simplicity and low cost of operation (Camel, 2000; Ganeshjeevan, Chandrasekar, Sugumar, Kadigachalam, & Radhakrishnan, 2005; Li, Wei, You, & Lydy, 2010) for solid samples. In static MAE, some compounds may be partly decomposed in high pressure and temperature conditions. In addition, when the extraction process finished, in order to avoid loss of volatile analytes, the vessels must be cooled to room temperature before being opened, and the extract should be filtered or centrifugated (Camel, 2000). In the recent years, dynamic microwave-assisted extraction (DMAE) has been applied for the sample pretreatment (Chen et al., 2008). The fresh solvent is continuously pumped through the extraction cell and analytes are transferred out of the extraction vessel as soon as they are extracted (Ericsson & Colmsjö, 2003). This is especially important to avoid degradation and contamination of analytes. Moreover, the extract could be online filtered and DMAE could be coupled with other sample pretreatment techniques.

The main aim of this work is to expand the applications of the CFME method to the extraction of organic compounds in complex solid matrixes. DMAE coupled with CFME in conjunction with GC–MS was first introduced and applied to the determination of OPPs in several vegetable samples. The fresh solvent was continuously pumped through the extraction vessel. The analytes were extracted from the vegetable sample, transferred from the extraction vessel to the chamber and then moved from extraction solvent into the microdop. After extraction, the microdrop was retracted back into the microsyringe and introduced into GC–MS system for analysis. The present method uses inexpensive apparatus, virtually eliminates solvent consuming, and combines extraction, separation, and preconcentration in one step. The method can achieve a rapid, simple, cheap and efficient extraction of pesticides in complex matrices.

2. Experimental

2.1. Chemicals and reagents

Eight OPPs, including demeton-s-methyl, phorate, diazinon, tolclofos-methyl, malathion, fenthion, quinalphos, and fenamiphos were purchased from National Institute of Metrology (Beijing, China), and the purity of OPPs is $\geqslant$98%. Stock solutions for the OPPs were prepared in hexane at 100 μg mL^{-1} and stored at 4 °C. Working standard solutions were prepared daily by diluting the stock solution with hexane. Analytical reagent grade sodium chloride, n-hexane, cyclohexane, dichloromethane, chloroform, carbon tetrachloride, ethyl acetate, and toluene were obtained from Beijing Chemical Factory (Beijing, China). Pure water was obtained with a Milli-Q water system (Millipore, Billerica, MA, USA). Quartz sand (25–50 mesh) was obtained from Sinopharm (Shanghai, China), which was heated in a muffle furnace at 550 °C for 1 h to eliminate organic substances before used.

2.2. DMAE–CFME system

A system of DMAE–CFME was assembled in our laboratory. The CFME unit used in this work is similar to that used elsewhere (Cao et al., 2008; Guo et al., 2005). The DMAE–CFME system consisted of a solvent storage container, a household microwave oven (NN-MX25WF, Shanghai, China) with the output maximum power of 800 W, and a microinfusion pump (Zhejiang University Medical instruments Co. Ltd., Zhejiang, China) for solution delivery, which can minimize the chance of producing the air bubble and make the organic microdrop more stable. A glass column (8.0 cm × 0.6 cm i.d.) was used as extraction vessel (Fig. 1(a)). A home-made glass extraction chamber (~0.8 mL) and a 10 μL GC microsyringe (Agilent Technologies Inc., California, USA) were used in microextraction unit (Fig. 1(b)). There was a cooling bath containing ice between CFME and DMAE unit. A minimum length of PTFE tube (i.d. 0.5 mm) was used for all connections.

2.3. Sample preparation

Fresh vegetable samples (cabbage, cauliflower, red cabbage, and cucumber) were purchased from local supermarket (Changchun, China). The samples were chopped and homogenized with food processor. The spiked samples were prepared by adding working standard solutions into the samples and stored for 24 h in the dark place at room temperature. Except for the experiments mentioned in Section 3.2.3, which were performed with all four samples, all other experiments were performed with cabbage. All experiments were performed in triplicate.

2.4. Extraction procedure

The extraction procedure of OPPs from vegetable sample was depicted in Fig. 1(c). Firstly, 2.0 g of sample was accurately weighted and mixed with 1.5 g of quartz sand used as dispersant. The resulting mixture was placed between two small plugs of glass fiber in the extraction vessel. Then the extraction vessel was put in the microwave oven. Aqueous solution containing 3% NaCl was used as extraction solvent and added in the solvent reservoir.

Subsequently, the microinfusion pump was firstly activated, and the extraction solvent was passed through the extraction vessel. The flow rate of extraction solvent was set at 1.0 mL min^{-1}. When the microextraction chamber was properly filled with the extraction solvent, 2.5 μL of microextraction solvent (toluene), was introduced into the extraction chamber with 10 μL microsyringe. The formed microextraction solvent drop can remain at the tip of the microsyringe. Then microwave irradiation was started with the power of 250 W.

Finally, after 10 min, the extraction was completed, and both microinfusion pump and microwave irradiation were switched off. The microdrop was retracted into the microsyringe and directly injected into the GC–MS for the analysis.

2.5. GC–MS analysis

A GC–MS system (GCMS-QP 2010 plus, Shimadzu, Kyoto, Japan) was used. 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 $\geqslant$ 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 1 min to 200 °C at a rate of 15 °C min^{-1} (held for 3 min), and then to 250 °C at a rate of 20 °C min^{-1} (held for 5 min), and then raised to 280 °C at a rate of 25 °C min^{-1} (held for 2 min). Injector temperature was maintained at 280 °C, and the injection volume was 1.0 μL in the splitless mode. The ion source and interface temperatures were 200 °C and 250 °C, respectively, and electron impact ionization energy was 70 eV. The mass spectrometer was operated in the selective ion monitoring (SIM) mode and the characteristic ions are given in Table 1. Full-scan MS data were