



Analytical Methods

Medium-assisted non-polar solvent dynamic microwave extraction for determination of organophosphorus pesticides in cereals using gas chromatography-mass spectrometry



Lijie Wu^a, Ying Song^a, Xu Xu^b, Na Li^a, Mingyuan Shao^a, Hanqi Zhang^a, Aimin Yu^a, Cui Yu^c, Qiang Ma^d, Chunmei Lu^e, Ziming Wang^{a,*}

^a College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China

^b Department of Chemistry, Liaoning University, Shenyang 110036, China

^c School of Chemical and Materials Engineering, Yanching Institute of Technology, Langfang 065201, China

^d Chinese Academy of Inspection and Quarantine, Beijing 100123, China

^e College of Technology Center, Jilin Entry-Exit Inspection and Quarantine Bureau, Changchun 130062, China

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ABSTRACT

A fast and green pretreatment method, medium-assisted non-polar solvent dynamic microwave extraction, was first applied to extract ten of organophosphorus pesticides (OPPs) from five cereal samples. Without adding any polar solvent, graphite powders (GP) were used as microwave absorption medium to transform microwave energy into heat energy. For recycling GP, an extractor was made by sealing GP inside the exterior tube of a glass sleeve. By dynamic microwave extraction using hexane as extraction solvent, ten OPPs could be extracted completely within 200 s, and the extract was directly analysed by GC-MS without any clean-up process. The effects of some experimental parameters on extraction efficiency were investigated and optimised. Relative standard deviations of intra- and inter-day ranging from 1.02% to 5.32% were obtained. Five real samples were analysed, and the recoveries obtained were in the range of 73.2–99.8%, and the relative standard deviations were lower than 6.63%.

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1. Introduction

Organophosphates are organic esters of phosphoric acid, thiophosphoric acid and other phosphoric acids, which have been widely used in agricultural fields to control pests, weeds, diseases and to increase harvest productivity for the last five decades (Otake et al., 2013; Rissato, Galhianega, Apon, & Arruda, 2005). However, it is well known that organophosphorus pesticides (OPPs) have a high acute toxicity due to the prevention of neural impulse transmission by their inhibition of cholinesterase (Fu et al., 2009; Sogorb & Vilanova, 2002). Recently, the researchers have found that most toxic incidents are linked with the intoxication of OPPs, especially OPP residues in vegetables, fruits and cereals (ICAMA, 2001; Koureas, Tsakalof, Tsatsakis, & Hadjichristodoulou, 2012). The European Union (EU) legislation has established maximum residue limits (MRLs) of the pesticides and the MRL is 0.01 mg kg⁻¹ for cereals (Regulation (EC) No. 396/2005). Therefore, the development of the fast, reliable and economically viable analytical

methods for the determination of OPP residues in foods and environmental matrices is of great significance.

Rice is a major food crop for more than 60% of the world population (Nguyen et al., 2008). The extraction of OPPs from rice samples can be achieved by conventional extraction techniques, such as solid-liquid extraction (Desmarchelier, 1980), Soxhlet extraction (Barceló, Solé, Durand, & Albaigés, 1991), mechanical shake-out extraction (Adachi, Ohokuni, & Mitsuhashi, 1984), ultrasonic extraction (Granby, Andersen, & Christensen, 2004), solid phase extraction (Liu, Liu, Ma, Liu, & Jia, 2006) and matrix solid-phase dispersion (Dórea, Sobrinho, & Braz, 2004) and so on.

In recent years, microwave-assisted extraction (MAE) has been widely used for extraction of OPPs in environmental samples, because of its main advantages, such as rapidity, simplicity, high extraction yields, low cost of operation and low solvent consumption. (Camel, 2000; Ganeshjeevan, Chandrasekar, Sugumar, Kadigachalam, & Radhakrishnan, 2005; Li, Wei, You, & Lydy, 2010). However, the effect of microwave energy chiefly depends on the nature of extraction solvent (Pastor, Vázquez, Ciscar & Guardia, 1997). Generally speaking, because polar solvents such

* Corresponding author. Tel.: +86 431 85168399; fax: +86 431 85112355.

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

as water, methanol and acetone can absorb more microwave energy (Ji, Deng, Zhang, Wu, & Zhang, 2007; Wang, Weller, Schlegel, Carr, & Cuppett, 2008), a wide range of polar and mixed solvents were used as extraction solvents. However, the extract obtained with polar solvent involves polar interferents, and the composition of extract is complex. In recent years, non-polar solvent has been successfully used in improved microwave-assisted extraction without adding any polar solvent (Yu et al., 2007). Because some kinds of carbon materials have excellent microwave absorbing capability, they have been the most promising materials (Li, Deng, Li, Ye, & Zhang, 2006; Lucchesi, Chemat, & Smadja, 2004; Xu & Lee, 2008). Wang, Ding et al. (2006a) first used microwave absorption medium (MAM) to replace water and other polar solvent to absorb microwave energy in dried samples (Wang, Wang et al., 2006b; Wang et al., 2006a). Yu et al. (2007) used non-polar solvent microwave extraction (NPSME) by adding the MAMs into the extraction system to extract essential oils from *Zingiber officinale* Rosc. (Yu et al., 2007). However, in most of reported methods, the MAMs including carbonyl iron powder (CIP), graphite powder (GP), activated carbon powder (ACP) and ionic liquid (IL) were directly added into samples, which lead to impossibility of the recycle of MAMs. For resolving this problem, Zhao et al. made a microwave absorption tube to protect MAM (Zhao, Xu, Su, Zhang, & Wang, 2012), but time and large volume of solvent consuming were inevitable when it was used in non-polar solvent microwave-assisted extraction of organophosphorus pesticides from fresh vegetable samples.

Dynamic microwave extraction (DME) has already been proved to be a quick, safe and efficient pretreatment method. So many applications of DME in various fields have been reported because it was especially beneficial to avoid degradation and contamination of analytes (Chen et al., 2009; Wang et al., 2010, 2011). Generally, polar organic solvent was necessary in DME, non-polar organic solvent that was used in DME can hardly be found in literatures reported.

In this study, a medium-assisted non-polar solvent dynamic microwave extraction (MA-NPS-DME) was assembled in our laboratory. An original extractor consisting of inner and exterior tube was first developed and used to heat sample and solvent with MAM under microwave irradiation. The exterior tube was full of GP and silica gel used to absorb microwave energy. Because of the protection of extractor, GP was not contacted with sample or solvent, therefore GP could be reused in MAE. Some experimental parameters which could affect the extraction efficiency were studied and optimised. The developed method was successfully applied to the analysis of real samples.

2. Experimental

2.1. Chemicals and reagents

Ten OPPs including demeton-s-methyl, phorate, diazinon, tebuipirimfos, chlorphrifos-methyl, tolclofos-methyl, pirimiphos-methyl, malathion, fenthion and sulprofos were purchased from National Institute of Metrology (Beijing China), and the purity of OPPs is $\geq 98\%$. Stock solutions for the OPPs were prepared in hexane at $100 \mu\text{g mL}^{-1}$ and can be stored at 4°C for two months. Working standard solutions were prepared daily by diluting the stock solution with hexane. Hexane, isooctane, petroleum ether and carbon tetrachloride were of analytical grade and purchased from Beijing Chemical Factory (Beijing, China). 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. MA-APS-DME apparatus

MA-NPS-DME was assembled in our laboratory (Fig. 1A). It mainly consisted of a solvent storage container, a household microwave oven (NN-MX25WF, Shanghai, China), a peristaltic pump (Michem Technology Co., Ltd., Beijing, China) and an extractor (Fig. 1B).

The extractor consists of inner and exterior tube. The internal diameter of inner and exterior tube is 6 mm and 14 mm, respectively, and the length of inner and exterior tube is 9.0 cm and 9.5 cm, respectively. GP was used as MAM. The exterior tube of the microwave extractor was filled with a mixture of GP and silica gel.

2.3. 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 ($30 \text{ m} \times 0.25 \text{ mm I.D.}$, film thickness of $0.25 \mu\text{m}$, J&W Scientific, Folsom, CA, USA). Helium (purity $\geq 99.999\%$) 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 to 140°C at a rate of $15^\circ\text{C min}^{-1}$ (held for 9 min), and then to 200°C at a rate of 3°C min^{-1} (held for 1 min), and then raised to 230°C at a rate of $15^\circ\text{C min}^{-1}$ (held for 2 min), finally, raised to 280°C at a rate of $25^\circ\text{C min}^{-1}$ (held for 2 min). Injector temperature was maintained at 280°C , and the injection volume was $1.0 \mu\text{L}$ in a 5:1 split ratio. The ion source and interface temperatures were 200°C and 250°C , respectively, and electron impact ionisation energy was 70 eV (Su et al. 2011). 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 acquired in the range of m/z 50–900 to obtain the fragmentation spectra of the analytes.

2.4. Sample preparation

Five kinds of cereal samples, including rice, maize, millet, broomcorn and sticky rice, were purchased from a local supermarket (Changchun, China). Cereal samples were powdered in a mill, passed through a 40 mesh sieve, and then stored in a sealed brown bottle at room temperature. The spiked samples were prepared by adding a reasonable amount of acetone to moisten the samples, spiking the stock standard solutions in the samples, shaking for 10 min and then standing for 12 h at room temperature. The rice sample was used in the optimisation of experimental conditions. All experiments were performed in triplicate.

2.5. MA-NPS-DME procedure

1.0 g of cereal sample was accurately weighed and mixed with 2.5 g quartz sand which was used as dispersant. The mixture was

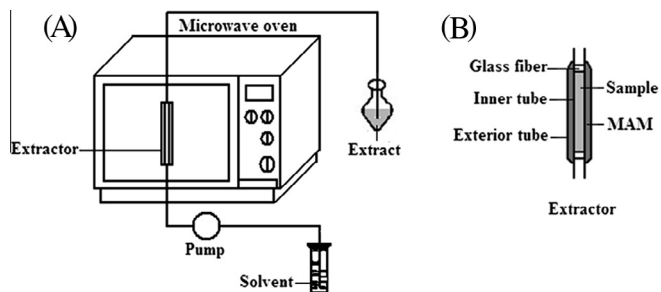


Fig. 1. MA-NPS-DME system (A) and the extractor (B).

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