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Full Length Research Paper

Determination of malathion and fenitrothion residues in wheat by solid phase microextraction/gas chromatography-mass spectrometery (SPME/GC-MS) method

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A solid phase microextraction (SPME) headspace sampling technique has been applied to gas chromatography / mass spectrometery for analysis of malathion and fenitrothion residues in wheat. Solid phase microextraction is an innovative solvent free technology that is fast, economical, simplicity and eco-friendly. The 65 µm polydimethylsiloxan (PDMS) fiber was used for the isolation of target compounds from wheat samples. The obtained recoveries of malathion were 91.1 and 104.12% and for fenitrothion were 98.9 and 101.2% for two fortification levels; 0.1 and 1 mg/kg, respectively. In some samples residues of malathion and fenitrothion showed different level of contamination, and in some samples no residues detected. Also, comparison of results with MRL showed that 4 samples have been residues more than MRL and other samples have been less than it. Finally, the results showed this method is good accuracy, precision and sensitivity for determination of residues of these organophosphorus pesticides in wheat.

Key words: Malathion, fenitrothion, residue, solid phase micro extraction (SPME), HS-SPME.

INTRODUCTION

Wheat is the most important cereal crop and constitutes the main component of millions of heads world over. Certain species of insects being able to be indirectly harmful for the man while attacking the agricultural crops. A large number of pesticides are in common use as grain protectants. Some pesticides such as malathion, have been used world wide for over 30 years, whereas others such as fenitrothion have been is use for 10 to 22 years (Tawab et al., 2007).

It was recognized that the subsequent residues of pesticides are a clear factor of contamination of food and of the biological food chain (Boussaahel et al., 2006). Various methods have been described for the extraction and determination of residues. For example gas chromatography applied for determination of pesticide residues in wheat flour (Anagnostopoulos and Miliadis, 2009).

Application of GC/NPD has been studied for the determination of residue levels of malathion and its metabolites and fenitrothion in post-harvest treated wheat during storage, milling and baking (Uygon et al., 2005). Some sample preparation procedures using solvents are time consuming, lab our intensive and multistage operations (Vas and Vekey, 2004).

Nowadays, it is necessary to employ innovative and fast method for pesticide residues analysis. Solid phase micro extraction (SPME) is a simple, low cost, rapid, selective and sensitive method. DI-SPME/GC-MS method used for analysis of MCPA residues in wheat (Krzyzanowski et al., 2008). Solid phase microextraction has been applied to the analysis of organophosphorus insecticides such as malathion and fenitrothion in fruits

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Table 1. Fortification levels and percent recoveries.

Pesticides	Fortification levels (mg/kg)	Mean recoveries for 3 replicates (%)
Malathion	0.1 , 1	91.1, 104.12
Fenitrothion	0.1 , 1	98.9 , 101.2

(Fytianos et al., 2006). Also, validation of an SPME method, using PDMS, PA, PDMS-DVB, CW – DVB SPME fiber coatings, for analysis of Organophosphoru s insecticides such as malathion and fenitrothion in natural waters has been studied (Lambropoulou et al., 2002). Headspace solid phase microextraction was used for evaluation of pesticide residue contents in cucumber and strawberry after washing treatment (Kin and Huat, 2010).

Also, headspace SPME method was applied for analysis of phosphine residues in wheat (Ren and Padovan, 2010). In this study a SPME headspace technique has been applied to the gas chromatography/ mass spectrometery (GC/MS) analysis of malathion and fenitrothion residues in wheat.

MATERIALS AND METHODS

Chemicals

Pesticide standards of malathion and fenitrothion were 99.8 and 99.2% of purity, respectively.

SPME procedure

The SPME procedure was performed using a manual SPME holder (Supelco) equipped with a 65 µm polydimethylsiloxan (PDMS) (Supelco) coating. Before the each use of the fiber was conditioned at the GC/MS injection port, at a temperature of 250°C for 90 min., to fully remove any contamination.

Wheat samples (sample preparation)

All determinations were performed using the polydimethylsiloxan (PDMS) 65 µm fibers. For evaluation of the recovery percentage and determination of the method, efficiency and sensitivity recovery test was performed. Recovery experiments were carried out in 2 fortification levels: 0.1 and 1 mg/kg, and for each level, with 3 replicates. Initially, 5.0 g of grounded wheat sample spiked with malathion and fenitrothion, separately, which the concentrations of the target pesticides in samples were 0.1 and 1 mg/kg. Wheat samples were transferred into the clear glass vials. Then, the SPME needle inserted to the vial and put on above the samples as HS-SPME method, vials put on the circulate bath for 15 min. [vapor pressure of malathion is 3.4×10^{-6} mmHg and for fenitrothion is 18 mPa (20°C)]. When the adsorption was completed, the fiber was withdrown into the vial and introduced into the GC/MS injector where the termal desorption of the analytes (desorption range 4 min at 250°C) was carried out. Finally, the amount of malathion and fenitrothion was detected.

GC/MS analysis

The GC/MS analysis was performed on a HP model 6890. The GC was equipped with capillary column DB_5 connected to the split/splitless injector mode. The optimized column temperature program was at first 80°C, then from 80 to 160°C (at 20°C/min).

Finally, from 160 to 210°C (at 5°C/min). The injector temperature was 200°C and detector temperature was 160°C. Helium was used a carrier gas.

RESULTS AND DISCUSSION

The focus of this work was to design a simple manual sampling technique for determination of malathion and fenitrothion residues in wheat. The analysis carried out showed that some samples were contaminated to malathion and fenitrothion residues. In addition, this study did not aim to detect the pesticides. In the recovery tests malathion pesticides are recovered in 91.1 and 104.12% and fenitrothion pesticide recovered in 98.9 and 101.2% for two levels. 0.1 and 1 mg/kg, respectively. Recovery results of two pesticides from fortified wheat grain are presented in (Table 1). Also, the results of the detector response and calibration curves showed in (Tables 2 and 3) and (Figures 1 and 2). Comparison of obtained results with codex MRLs showed that some samples have the residues of these pesticides more than codex MRLs and some samples have been less than codex MRLs.

Also, in some samples these pesticides were not detected. Results showed that HS-SPME is an appropriate method for investigation of these pesticide residues in wheat. This method is fast and low cost and can be performed in the short time. As the main trait of this method, there is no need for the solvents.

Finally, this method is an appropriate technique that can be used for determination of malathion and Fenitrothio

Conclusion

This study of SPME procedure with headspace sampling showed that the use of this method is very useful for determination of target organophosphorus pesticides namely malathion and fenitrothion in wheat samples. In addition, the developed method of HS-SPME with GC/MS is suitable, rapid and precise to this purpose.

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Table 2. Evaluation of detector response for malathion.

Peak area	Concentration (mg/kg)
82446	100
7984	10
732	1
83	0.1
26	0.01

Table 3. Evaluation of detector response for fenitrothion.

Peak area	Concentration (mg/kg)
104884	100
51743	50
4799	5
982	1
79	0.1
42	0.01

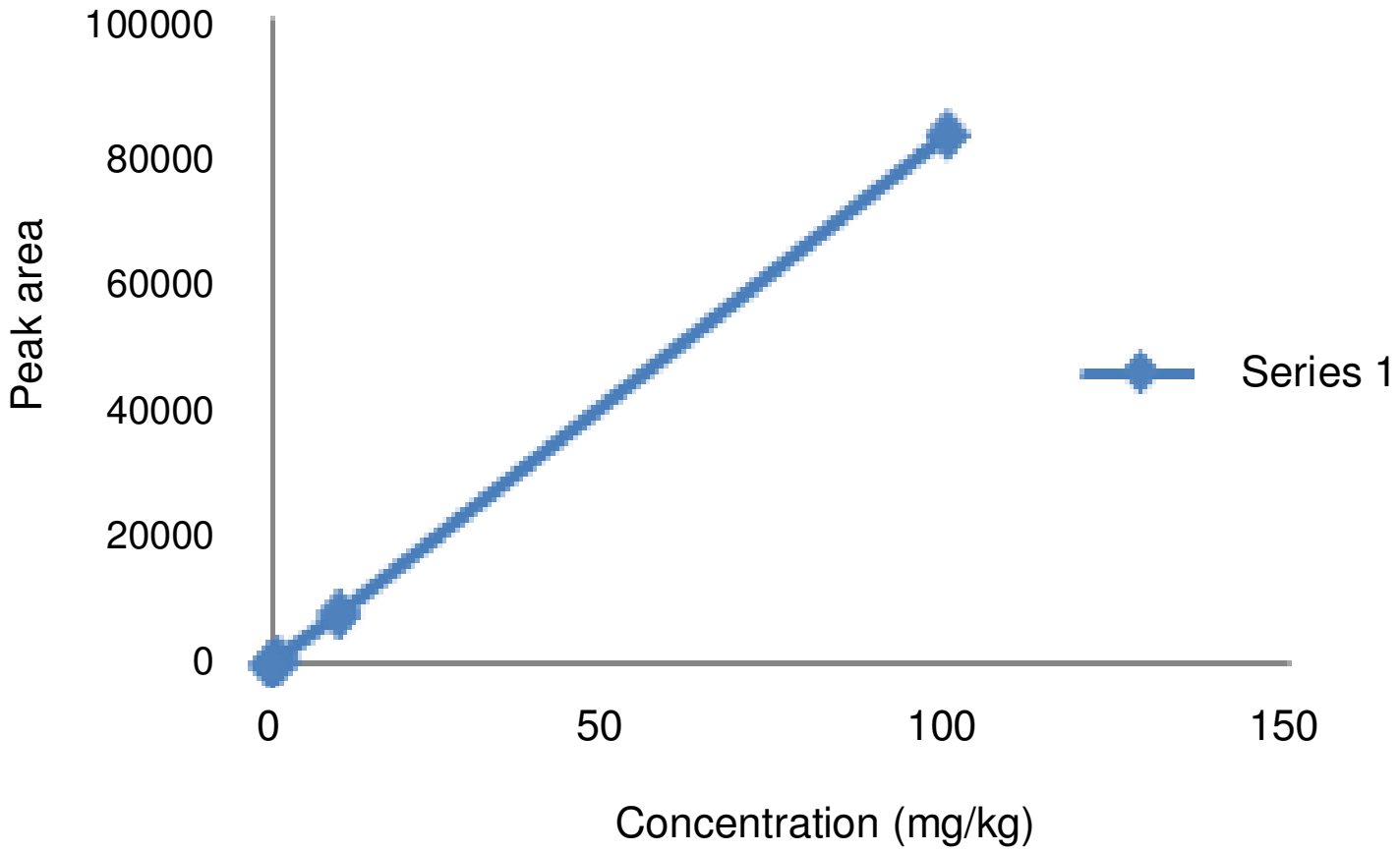

Figure 1. Calibrathion curves for malathion.

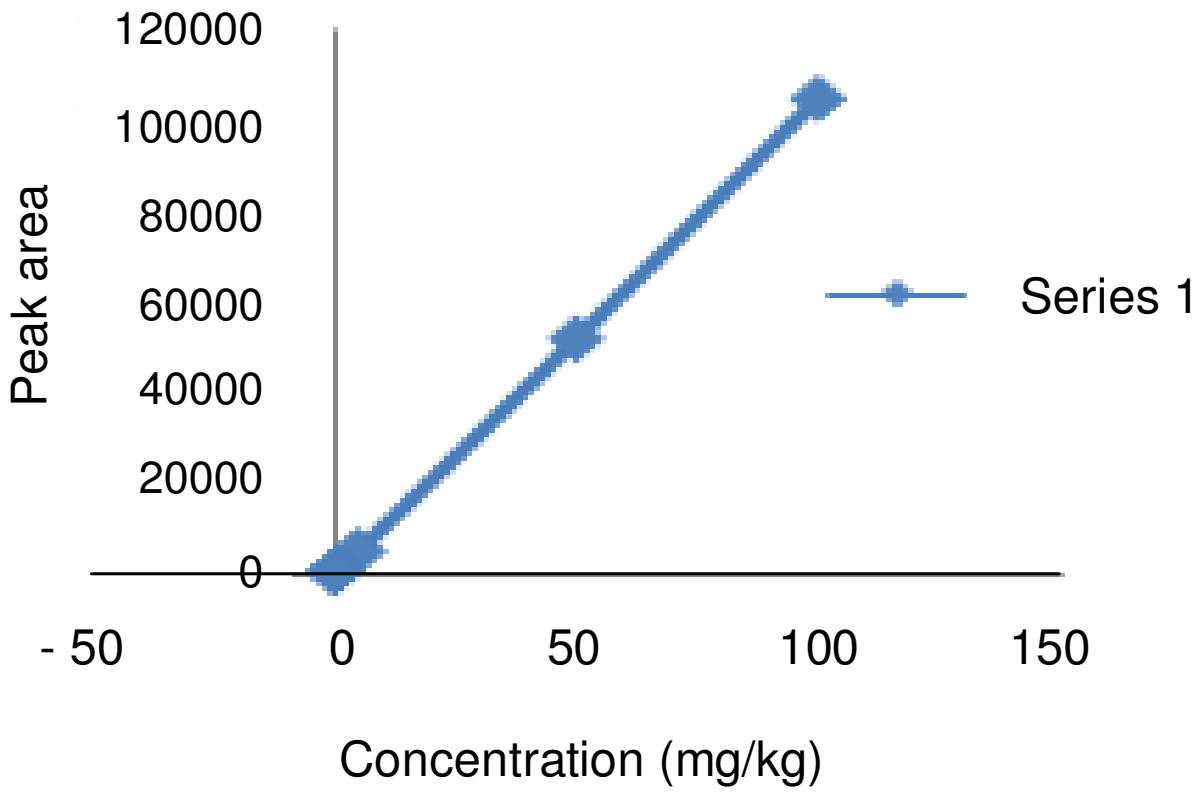

Figure 2. Calibration curves for fenitrothion.

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