Application of Solid Phase Microextraction to the Analysis of Pesticides in Vegetables

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ABSTRACT

Solid phase micro-extraction (SPME), a solvent-free, rapid and inexpensive method for the extraction of organic compounds from aqueous sample matrices, was evaluated for determinat ion of the 120 pesticides in vegetables such as crown daisy, perilla leaf, leafy lettuce and to mato. The analysis conditions were chosen for the SPME method:15 min of immersion of the PDMS fiber in 10 ml of the solution with stirring at 1,000 rpm. The recovery tests were ca rried out in triplicate. The range of recoveries was 0~142% for organochlorine pesticides and 4.9~200% for organophosphorus pesticides. The recoveries were very low in the pesticide gr oups with low solubility in water. The recoveries became lower in proportion to the interferen ce materials in vegetables. The recovery in tomato was relatively higher than that in perilla le af and crown daisy. The recovery values obtained by SPE and SPME were compared. In leaf y lettuce, recovery obtained by SPE method ranged from 58.1% to 136.1% and recovery by SPME ranged from 9.6% to 176.3% in organophosphorus pesticides. The recovery in SPME method was satisfactory with 136% for ethoprophos, 119% for methidathion and 113% for dia zinon. Meanwhile, recovery of EPN, phenthoate and 2,4-DDT revealed relatively low value of 38%, 41% and 3.4%, respectively. However, most of pesticides applied to SPME method sho wed constant recovery and precision. From these results, it can be concluded that solid phase micro-extraction might be an appropriate method for the screening test of pesticides in veget ables.

INTRODUCTION

Solid phase micro-extraction (SPME), first introduced by Arthur and Pawlizyn in 1990, is a solvent-free, rapid and inexpensive method for the extraction of organic compounds from aq ueous sample matrices. A fused silica fiber coated with a polymeric film is exposed to the li quid of extraction and the extracted organic substances accumulated in the stationary phase ar e thermally desorbed in the injector of the gas chromatography. Comparing with traditional liq uid-liquid and solid phase extraction methods, SPME needs neither purification nor a concentr ation step for sample preparation and thus enabled us to shorten time required for analysis. S

PME has been successfully applied to the analysis of both polar and non-polar compounds in cluding volatile organic compounds, phenols, and PAHs/PCBs from solid, liquid, or gas phase. Also, SPME has been extensively used for the analysis of pesticide residues from simple aq ueous samples. However, there is few report on analysis of pesticide residues in agriculture pr oducts, because of the complex matrices causing interference in the extraction procedure. In th at viewpoint, we analyzed pesticides in vegetables such as leafy lettuce, perillar leaf, tomato a nd crown daisy using SPME method, and the results will be described in this paper.

EXPERIMENTAL

1. Materials

Pesticide standards were purchased from Ridel-de Haen Co. Ltd., (Germany). All solvents wer e grade for pesticide residue. SPME holder and fiber assemblies for manual sampling were ob tained from Supelco. 100μm PDMS fiber and PA fiber were used. Fibers were conditioned in hot injection port of GC for overnight. Gas chromatography analysis were carried out in HP 6890 equipped with ECD and NPD detector.

2. Sample preparation

Approximately 1 kg of sample was chopped and 30 g was accurately weighed for analysis. A 50 ml volume of acetonitrile was added and the resulting mixture was blended for 2 min at high speed. The homogenate was then filtered into glass container containing *ca.* 5 g of Na Cl and the container was shaken vigorously for at least 1 minute and allowed to phase separ ation for about 30 min. After separation, 100 μl of upper layer was transferred to the 12 ml septum cap vial containing a magnetic bar and the final volume was adjusted to 10 ml with water. SPME fiber was introduced and exposed to the solution while stirring at *ca* 1,000 rpm. After an adsorption for 15 min at room temperature, the fiber was immediately injected into gas chromatography.

3. Gas chromatography analysis condition

HP-5 (30 m×320 μm ID×0.25 μm film thickness) column was used for the analysis of organoc hlorine pesticides and oven temperature was programmed to 150°C (2 min), 150°C to 240°C at 8 °C /min, 240°C (2 min), 240°C to 280°C at 15°C /min, and 280°C (5 min).

The Injector temperature was set to 230°C and the ECD detector temperature was 290°C. Car rier gas was nitrogen with 1.5 ml/min. For the analysis of organophosphorus pesticides, HP-5 column (30 m×320 μm ID×0.25 μm film thickness) was employed and oven temperature was programmed t

o 100°C (2 min), 100°C to 140°C at 10°C /min, 140°C to 200°C at 10°C /min, and 200°C (3 min). The Injector temperature was adjusted to 210°C and the NPD detector temperature was set to 280°C. Carrier gas was nitrogen with 1.5 ml/min, hydrogen with 20 ml/min, and air wi th 60 ml/min.

RESULT AND DISCUSSION

The experiment was carried out to find optimum conditions for SPME using mixed standard s olution. The following parameters were adjusted to optimize extraction condition: the type of fiber, the speed of stirring, and immersing time. Two types of fiber with different absorbent p hases were used: 85 μm PA-fiber and 100 μm PDMS-fiber. There was a slight difference in s electivity depending on the polarity of each pesticides, but no significant difference between t hose two fibers. In case of immersing time, extraction efficiency increased sharply between 1 min and 15 min. There was no significant increase after 15 min. As the speed of stirring inc reased, the efficiency of extraction was increased. The speed of stirring played an important r ole in reaching the equilibrium of partition. In addition, it was very important to maintain a constant stirring speed and immersion time in order to obtain reproducible results. From these results, the following conditions were chosen for the analytical method: 15 min of immersion of the PDMS fiber in 10 ml of the solution with stirring at 1,000 rpm. For the assessment of validity of SPME in vegetables, the recovery of 120 different pesticides was determined by multi-residue method. In addition, to evaluate the precision of the method, spiked samples w ere analysed in triplicate. The vegetables used for recovery tests were crown daisy, perilla lea f, korean lettuce and tomato. The range of recoveries was 0~142% for organochlorine pesticid es and 4.9~200% for organophosphorus pesticides. In the pesticide groups like DDT and pyret hroids with low solubility in water, the recoveries were very low. Most of pesticides in stand ard solution had a significant adsorption ability to fiber. But, when the sample was spiked, th e recoveries became lower in proportion to the interference materials in vegetables. The recov ery in tomato was relatively higher than that in perilla leaf and crown daisy. The recovery va lues obtained by SPE and SPME were compared. In leafy lettuce, recovery obtained by SPE method ranged from 58.1% to 136.1% and recovery by SPME ranged from 9.6% to 176.3% i n organophosphorus pesticides. The recovery in SPME method demonstrated significant differe nces according to the kinds of pesticides in comparison with SPE method. The recovery in S PME method was satisfactory with 136% for ethoprophos, 119% for methidathion and 113% f or diazinon. Meanwhile, recovery of EPN, phenthoate and 2,4-DDT revealed relatively low val ue of 38%, 41% and 3.4%, respectively. However, most of pesticides applied to SPME metho d showed constant recovery and precision. From these results, it can be concluded that solid

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