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Electrically assisted solid-phase microextraction combined with liquid chromatography–mass spectrometry for determination of parathion in water

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ABSTRACT

A novel method for electrically assisted microextraction coupled to liquid chromatography–mass spectrometry was evaluated for determination of trace levels of parathion in water. A pencil lead electrode was used in a di-electrode system to extract parathion onto the electrode surface with a reductive potential applied. The optimum extraction conditions were found to be a potential of −600 mV for 60 s in pH 2 phosphate buffer solution. The parathion was desorbed statically for 1 min and dynamically for 3 min in the commercial SPME–HPLC desorption chamber, then analyzed with LC–APCI–MS/MS. The detection limit (LOD) for parathion in water was found to be 0.3 ng/mL. The proposed technique was demonstrated to be fast, sensitive and not require a solvent sample pretreatment.

1. Introduction

Most pesticides spread in agricultural applications cause environmental contamination of water, air and soil. Organophosphorous pesticides have been used widely in animal husbandry, crop protection and elimination of ectoparasites. Parathion is one of the most important organophosphorous pesticide compounds (OPs). The structure of parathion is shown in Fig. 1. It consists a thiophosphoric moiety linked to a nitrobenzene group. Its toxicity is primarily associated with inhibition of acetylcholinesterase (AChE) activity. It is absorbed quickly through the skin and eyes [1,2]. Therefore, monitoring traces of parathion in water is important [3].

Various analytical techniques have been used for determination of parathion in the environment, mainly employing chromatographic approaches, including gas chromatography–mass spectrometry (GC–MS) [4–8], liquid chromatography–mass spectrometry (LC–MS) [9,10], ion-mobility spectrometry coupled with mass spectrometer (IM-MS) [11] and capillary electrophoresis [12]. Electrochemical detection methods also are suitable for analysis because of desirable features of electrochemistry [13–17]. Although gas chromatographic methods frequently were applied for analysis of parathion, liquid chromatography often is preferred because of decreased restrictions on volatility.

Sample pretreatment is an important part of the proposed method. Various sample techniques were used to accurately determine parathion at trace levels in complicated matrices. Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are generally used in analysis of parathion in water samples [18–21]. Because many organic solvents are required, this represents a threat to the environment and technician health in the laboratory. Solid-phase microextraction (SPME) has recently become popular because of the reduction in solvent use and exposure. Solid-phase microextraction (SPME), developed by Pawliszyn and colleagues in 1989 [22], was widely used for analytical toxicology [23], food [24–26] and environment [27] analysis. The detection limit of SPME can reach the ng per L^{-1} level. This technique is based on the distribution of analyte between the extracting phase and the matrix. SPME has advantages of simplicity, ease of use and concentration. New fibers of SPME techniques have been developed, such as different material of fiber (e.g. pencil lead) [28–32], surface adsorbent modification [33–36], electrochemically-controlled solid-phase microextraction (EC-SPME) [37–39]. An important aim of these improvements was to increase the efficiency of extraction and to improve the selectivity of SPME. However, some drawbacks have included fiber fragility, short fiber life-time, and a more expensive and longer equilibration time.

The purpose of this study is to develop electrically assisted solid-phase microextraction combined with LC–APCI–MS/MS for determination of parathion in environmental water. The main idea of this project was to focus on utilizing electrochemistry as a concentration approach. The pencil lead played two roles: an extraction fiber and a cathode. Pencil lead is a porous material that can provide very large surface area, enabling the electrochemical reac-

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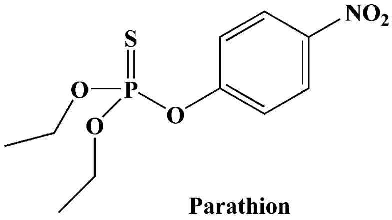

Fig. 1. The chemical structure of parathion.

tion. The preconcentration of parathion from the matrix occurred when a suitable reductive potential was applied to the electrode. The optimal parameters affecting extraction efficiency, including extraction potential, adsorption time, pH value and the stirring rate were studied. The performance of electrically assisted-SPME-LC–APCI–MS/MS to analyze parathion in water samples also was evaluated.

2. Experimental

2.1. Chemicals and reagents

The parathion used in this experiment was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The organic solvents and hydrochloride (HCl) were obtained from Merck (Darmstadt, Germany). All chemicals used in this study were analytical reagent or HPLC grade. The water was purified in the laboratory (>18 MΩ) using RiOs™ 3 Water Purification Systems from Millipore Co. (Bollerica, MA, USA). The stock solution of parathion was prepared in methanol and stored at 4 °C in a refrigerator. The phosphate buffer solution consisted of 10 mM disodium hydrogen phosphate (Na_2HPO_4) and potassium dihydrogen phosphate (KH_2PO_4). The pH values of the phosphate buffer solutions were adjusted by altering the ratio of 10 mM Na_2HPO_4 and KH_2PO_4 solution.

2.2. Analytical conditions

The chromatographic system used was a Dynamax ProStar 210 liquid chromatograph (Thermo Finnigan, San Jose, CA, USA), employing two LC pumps. The parathion was separated on a ZORBAX 80 Å Extend-C18 LC column (15 cm × 2.1 mm, 5 μm) (Agilient Technologies, Palo Alto, CA, USA). Mobile phases A and B were water solution with 0.1% acetic acid and methanol with 0.1% acetic acid, respectively. The LC program was the isocratic elution at 90% of solvent B for 3 min and the flow rate of mobile phase was 500 μL/min.

A Varian 1200L triple-quadrupole LC/MS (Varian, Walnut Creek, CA, USA), equipped with an APCI source was used for the determination of parathion. The optimum voltages were found by tuning with an automated procedure that maximized the signal for the ions of parathion. The instrument conditions were described as follows: vaporizer temperature, 550 °C, drying gas temperature, 350 °C, drying gas pressure, 33 psi, nebulizer gas pressure, 30 psi, auxiliary gas pressure, 1.7 psi, shield voltage 450 V and corona current 3 μA. For quantitation, selected reaction monitoring (SRM) was used to increase the sensitivity and selectivity for trace parathion. During the SRM analysis mode, mass peak width was 2.0 Th for Q1 and 1.0 Th for Q3. The collision gas was argon at a pressure of 2.0 mtorr.

2.3. Extraction procedure

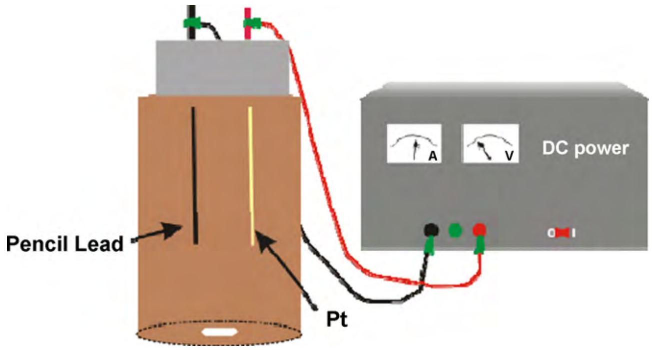

Fig. 2. Schematic of electrode microextraction device.

The extraction device shown in Fig. 2 was constructed in the authors laboratory. A pencil lead HB (5.5 cm × 0.3 mm) (Pilot Co., Tokyo, Japan) was purchased from the commercial market. It was used as a cathode while platinum was used as an anode in the two electrode system. Both electrodes were fixed by the septum at a distance of 1 cm. The DC power supply unit was purchased from SANCO Electronics Co., Ltd. (Ningbo, Zhejiang, China) and used to adjust the potential. Cyclic voltammetric (CV) measurement of parathion was performed with a BAS Epsilon electrochemistry workstation (Bioanalytical Systems, West Lafayette, IN, USA). The three electrode system used a pencil lead as the working electrode, Ag/AgCl as a reference electrode and platinum as an auxiliary electrode. Before electrochemical analysis, deoxygenation was performed by purging with high-purity nitrogen (>99%) for 10 min.

The extraction procedure was performed as follows: 5 mL of a water sample containing parathion adjusted to pH 2 was added to 5 mL brown glass vial. A PTFE/silicone septum was used to hold the pencil lead and platinum electrode. Before performing experiment, the electrode was inserted into aqueous phosphate buffer solution of pH 2 until the current was stable. Then two electrodes were transferred to the solution containing parathion. A DC potential was applied on the electrodes at −600 mV for 60 s. When the extraction was complete, the pencil lead was transferred to the SPME/HPLC desorption chamber (Supelco, Bellefonte, PA, USA). The compound was desorbed with 200 μL methanol in static desorption mode for 1 min, in dynamic mode for 3 min with mobile phase and then detected by LC–APCI/MS/MS.

2.4. Water sample analysis

River water and ground water were collected from Taichung city, in central Taiwan. Before storing at 4 °C in the refrigerator, the samples were acidified with 0.1N HCl and the pH was adjusted to 2. Prior to analysis, the water sample was filtered with a 0.22 μm syringe filter (Millipore, Billerica, MA, USA). 5 mL samples were taken with the home-made extraction system, then the analyte was extracted under the optimum conditions of electrode microextraction. Finally, the extract was analyzed by LC–APCI–MS/MS.

3. Results and discussion

3.1. Electrochemical behavior of parathion on the electrode and its mass spectrum

The electrochemical characteristics of parathion at the pencil lead working electrode were studied first. The continuous cyclic voltammetric (CV) response of 1 μg/mL parathion on the pencil lead electrode in pH 2.0 phosphate buffer was measured at a scan rate of 100 mV/s over the range of +0.6 to −0.6 V. The cyclic voltammogram is shown in Fig. 3. The results indicate that the first cathodic peak at −400 mV in curve A is due to four-electron reduction of parathion with irreversible transformation from the φ-NO_2 into φ-NHOH. In a preliminary experiment, the pencil lead was held at a