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Short communication

Development of a novel solid-phase extraction element for thermal desorption gas chromatography analysis

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Abstract

A novel solid-phase extraction element is developed for sorptive enrichment of dilute analytes from liquid samples with high extraction efficiencies due to its larger amounts of polydimethylsiloxane (PDMS) absorbent than the conventional syringe type of solid-phase microextraction (SPME). The extraction element is made of titanium (Ti) open tubular tube (30 mm × 1.2 mm i.d. × 1.6 mm o.d.) coated with a chemically bonded layer of PDMS (500 μm in thickness). The extraction element combined with thermal desorption–gas chromatography–mass spectrometry using a pyrolysis–gas chromatography–mass spectrometry system was used to extract and analyze a typical herbicide, bethrodine in water samples over a concentration range from 2.5 to 2.5×10^4 ng/l. Thus obtained calibration curve showed good linearity for the tested whole concentration range with regression coefficient of 0.992. Detection limit of 0.5 ng/l level was achieved and the reproducibility of the measurements for bethrodine at 10 ng/l level was found to be fairly good with relative standard deviation below 7.5%.

Keywords: Thermal desorption; Solid-phase extraction; Instrumentation; Polydimethylsiloxane; Pesticides; Bethrodine

1. Introduction

Solid-phase microextraction (SPME) as a simple and rapid extraction technique is widely used in various areas for extracting dilute analytes from both liquid and gaseous samples because of its high extraction efficiency and no requirement of solvents in extraction step [1,2]. Recently, a stir bar sorptive extraction (SBSE), namely a stir bar coated with 100% polydimethylsiloxane (PDMS), is reported to obtain high extraction efficiency especially for trace organic compounds in aqueous samples [3]. However, the SBSE procedure sometimes suffers from its fragility due to the use of glass tube covering a magnetic bar and the peeling of the PDMS surface coating during repeated sorption, desorption and/or cleaning steps. In this work, a novel solid-phase extraction element named "Magic Chemisorber" (MC) is developed to overcome these problems. The MC consists of a titanium (Ti) open tubular tube (30 mm × 1.2 mm i.d. × 1.6 mm o.d.), whose inner and outer surfaces are deactivated in the same way developed for deactivation of stainless steel capillary column [4,5], and coated with the same length of PDMS tube. Its surface between outer of Ti tube and inner surface of PDMS tube is further chemically bonded with PDMS. Thus the element is rugged and suitable for repeated use. The main objective of this work is to illustrate this extraction element combined with thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) using a pyrolysis–GC–MS (Py–GC–MS) system can be used to analyze trace amounts of a herbicide, bethrodine, in water samples.

2. Experimental

2.1. Preparation of the solid-phase extraction element: "MC"

The MC consists of a deactivated Ti capillary tube (30 mm × 1.2 mm i.d. × 1.6 mm o.d.; Frontier Labs.,

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Fukushima, Japan) and a thick layer of PDMS (0.5 mm film thickness). The outer and inner surface of Ti tube was deactivated by the deposition of silicone layer [5] and additionally treated with octamethylcyclotetrasiloxane [6]. Furthermore, all surface of the Ti-tube was coated with 1% of dicumylperoxide solution (dichloromethane as solvent) and dried at room temperature. Then it was covered with the same length of a commercially available PDMS tube (1.6 mm i.d. × 2.1 mm o.d.; Nipon Rika Kogyo, Tokyo, Japan) and heated at 200 °C for 1 h to yield chemical bonding between Ti tube and PDMS to form the immobilized PDMS layer. Finally the MC was cleaned up through Soxhlet extraction with hexane solvent, conditioned from 50 to 280 °C at a rate of 40 °C/min with holding at 280 °C for 10 min under a helium carrier gas flow and then cooled down to room temperature.

2.2. Reagents and sample solutions

A typical herbicide, bethrodine (*N*-butyl-*N*-ethyl-α,α, α-trifluoro-2,6-dinitro-*p*-toluidine, $C_{13}H_{16}O_4N_3F_3$; molecular mass: 335.3, CAS No. 732-11-6; GL Science, Tokyo, Japan) was selected as the test component.

A working standard solution containing bethrodine at approximately 10 mg/l was adjusted by acetone. Furthermore, a series of aqueous standard solutions were prepared by spiking an appropriate amount of the working standard solution into distilled water. Water standard samples (20 ml each) were prepared over a concentration range from 2.5 to 2.5×10^4 ng/l in this work.

2.3. Instrumentation

Fig. 1 shows a schematic diagram of the Py–GC–MS system for TD–GC–MS measurements using the MC extraction element. The main apparatus employed in this work consists of a double-shot pyrolyzer (Frontier Labs., Model PY-2020iD), and a GC–MS system (Shimadzu, Kyoto, Japan; Model GCMS-QP2010) equipped with a deactivated metal capillary column (Frontier Labs., Ultra ALLOY-5, 30 m × 0.25 mm i.d.) coated with cross-linked 5% diphenylpolydimethylsiloxane of 0.25 μm film thickness. The outlet of the pyrolyzer was directly connected to a heated split/splitless injection port and the thermally desorbed analytes flow into the capillary column by 1/5 of split ratio using helium carrier gas.

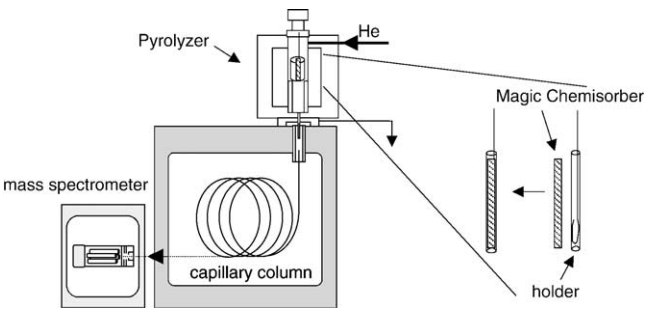

Fig. 1. Schematic diagram of the TD–GC–MS system.

2.4. Extraction

The MC was preliminarily conditioned from 50 up to 280 °C at a rate of 40 °C/min with holding at 280 °C for 10 min under the helium carrier gas flow in the pyrolyzer and then cooled down to room temperature. Then, it was immersed into 20 ml of the aqueous sample solution and stirred with a Teflon coated magnetic stirrer chip for a fixed extraction time. After extraction process, the MC taken out of the solution was transferred into a sample holder (deactivated stainless steel cup, 8 mm length, 3.8 mm i.d., 0.1 mm thickness; Frontier Labs.) after wiping water on its surface with a piece of Kimwipe paper, and subjected to the following TD in the pyrolyzer.

2.5. TD-GC/MS measurements

The MC placed in a holder was heated in the pyrolyzer from 60 to 280 °C at a heating rate of 40 °C/min and maintained at 280 °C for 8.5 min. Thus the thermally desorbed trace components were dynamically trapped into the head of the separation column with a helium flow at a rate of about 1 ml/min at GC initial oven temperature of 40 °C. Then, the column temperature was programmed from 40 to 280 °C at a rate of 20 °C/min and held at 280 °C for 10 min. For the MS measurement, ionization was carried out by electron impact (EI) at 70 eV and electron multiplier voltage was 1 kV. Selected ion monitoring (SIM) acquisition was carried out by monitoring the specific ion peak of bethrodine at *m*/*z* 292 with 200 ms of dwell time.

3. Results and discussion

The effects of various factors, such as the thermal desorption temperature and time from MC, and the extraction time into MC, which affect the extraction efficiency of analytes were studied. First, the thermal desorption conditions were empirically examined by using evolved gas analysis (EGA) [7] of bethrodine in MC using the TD–GC–MS system. Here, a MC extracting bethrodine from 5 ml of water containing bethrodine (40 μg/l) for 60 min was subjected to EGA. Fig. 2 shows a typical EGA curve of bethrodine obtained when desorption temperature was increased from 50 to 280 °C at a heating rate of 40 °C/min using SIM acquisition (*m*/*z* 292). As shown here, the thermal desorption began at about 80 °C (0.75 min), showed its maximum intensity at ca. 220 °C (4.25 min) and came back to the baseline in 11 min. Considering this EGA profile, the TD condition was fixed from 60 to 280 °C at a heating rate of 40 °C/min and empirically maintained at 280 °C for 8.5 min. Therefore the total TD time was 14 min.

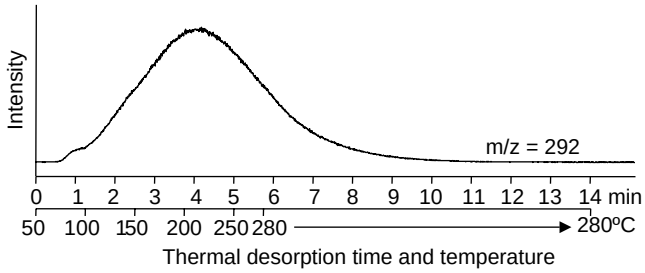

Fig. 2. A typical EGA curve of bethrodine in MC extracted for 60 min from 5 ml of water spiked with bethrodine (40 mg/l) obtained when the desorption temperature was increased from 50 to 280 °C at a heating rate of 40 °C/min using SIM acquisition (*m/z* 292).

Then the extraction time required for quantitative extraction of bethrodine in water was examined. Fig. 3 shows an effect of extraction time for bethrodine into MC from the sample water (20 ml) at a concentration of 2.5 μg/l of bethrodine between 15 and 60 min under stirring on peak intensity of bethrodine observed by TD–GC–MS measurements under the optimum TD conditions. As shown in this extracting time profile, the peak intensity with the increase of the extraction time up to 45 min and then showed a plateau. This fact proved that the time required for reaching the equilibrium of bethrodine between the aqueous and the stationary phase was about 45 min. Therefore an extraction time of 60 min was selected for the following procedure.

Under the optimum extraction and desorption conditions, the linearity and detection limit of the method were tested using 20 ml distilled water spiked with various amounts of bethrodine. Fig. 4 shows a typical calibration curve for bethrodine at a concentration range from 2.5 to 2.5×10^4 ng/l with regression coefficient of 0.992, showing a wide dynamic range over 10^4. Fig. 5 shows a typical mass chromatogram obtained for 20 ml distilled water spiked with bethrodine at a concentration of 2.5 ng/l. The detection limit calculated from the S/N ratio obtained for this chromatogram was less than 0.5 ng/l. A relative standard deviation (R.S.D.) of less than 7.5% were obtained for five repeated runs at 10 ng/l level, illustrating the practical effectiveness of the method.

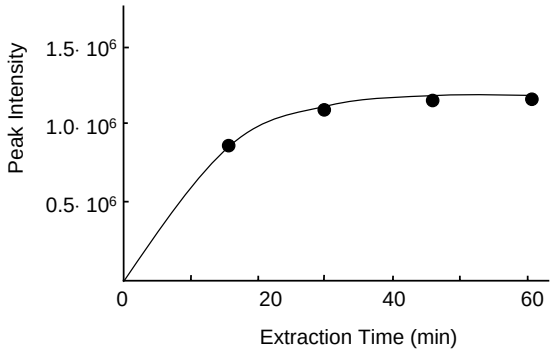

Fig. 3. Effect of extraction time on peak intensity of bethrodine in 20 ml of water containing 2.5 mg/l of bethrodine obtained by TD–GC–MS using MC.

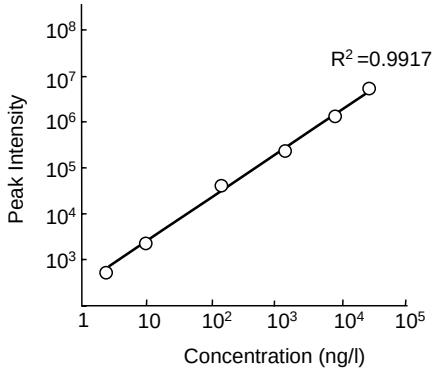

Fig. 4. A typical calibration curve obtained for distilled water samples spiked with bethrodine at a concentration range from 2.5 to 2.5×10^4 ng/l.

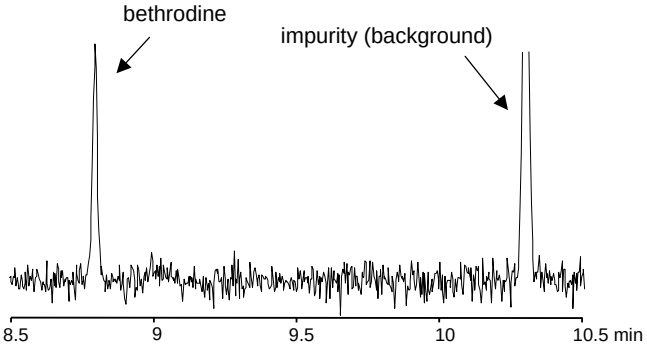

Fig. 5. A typical mass chromatogram obtained for a distilled water spiked with bethrodine at a concentration of 2.5 ng/l using SIM acquisition at *m/z* 292.

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