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Talanta

journal homepage: www.elsevier.com/locate/talanta

Novel unbreakable solid-phase microextraction fibers on stainless steel wire and application for the determination of oxadiargyl in environmental and agricultural samples in combination with gas chromatography–mass spectrometry



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ARTICLE INFO

Article history:

Received 9 February 2014

Received in revised form

28 April 2014

Accepted 30 April 2014

Available online 13 May 2014

Keywords:

Solid-phase microextraction

Sol–gel

Gas chromatography–mass spectrometry

Oxadiargyl

Environmental samples

Agricultural samples

ABSTRACT

Sol–gel based solid-phase microextraction fibers supported by a stainless steel wire were fabricated and employed for GC–MS determination of oxadiargyl in real samples. The fibers were based on four compounds with different polarity: polar and non-polar (end-capped) poly(dimethylsiloxane) (PDMS), polyethylene glycol (PEG), and poly(ethylene-propyleneglycol)-monobutyl ether (UCON). For this purpose, the surface of the stainless steel was initially modified by (3-mercaptopropyl) trimethoxysilane. The results of the modification procedure were evaluated by cyclic voltammetry and energy dispersive X-ray (EDX) spectroscopy. After the modification, four different sol–gel based SPME fibers with different values of polarity, polar and non-polar PDMS, PEG, and UCON have been prepared and investigated. They are supposed to be employed to determinate oxadiargyl in agricultural and environmental samples prior to gas chromatography–mass spectrometry analysis. Most important parameters that affect the extraction efficiency were also optimized. Under optimized conditions, the proposed method was found to be linear for the concentrations ranging from 100 ngL⁻¹ to 2 mgL⁻¹ with R² = 0.997. Limit of detection (LOD) of 40 ngL⁻¹ and relative standard deviation of less than 10% were obtained. Relative recovery in environmental and agricultural samples was in the range of 73–96%.

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1. Introduction

Solid-phase microextraction (SPME) is a simple sampling and sample preparation method that combines extraction, pre-concentration and sample introduction in one step, does not require the use of solvents, and permits desorption directly into the injector of the chromatographic systems [1–4].

In SPME, extraction is conducted by a thin film of coated materials on a solid support. Several fiber coatings with different values of polarity are commercially available [5–10]. However, they exhibit drawbacks such as fragility, which necessitates taking extra care during usage. Moreover, the fibers do not have a resistance to high temperature and tend to swell in organic solvents [11]. In recent years, a new generation of super elastic SPME fiber assemblies have been commercialized. However, the latter are expensive. To overcome the fragility of fused silica, commonly

used as the support for polymeric coatings in SPME applications, other materials, mainly metallic wires such as platinum [12–15], anodized aluminum [16], gold [17,18], copper [19], titanium [11,20], and nickel–titanium alloys [21–26], have been proposed to substitute the silica rod.

Application of stainless steel wires as substrate for SPME fiber coating has been reported elsewhere [27–34]. In these applications, the fiber coatings have been assembled using different techniques such as physical deposition, electrochemical deposition, adhesive methods, and sol–gel technology. Besides these technologies, sol–gel based methods have gained increasing attraction due to their simplicity, flexibility for coating composition and operational stability of the coating [35]. In a sol–gel process, the surface area of the solid support should endorse the growth of the polymeric chain. In the above mentioned reported works, stainless steel has been directly used as a support, though it is known that the surface density of hydroxyl groups is not sufficiently high to ensure a uniformly bonded coating to be obtained [36].

Rice cultivation is an economically important agricultural activity in many areas around the world. To control weed growth,

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many kinds of herbicides are directly applied on the flooded soil. Therefore, tracing these chemicals and studying their chemical interactions in soil and aqueous solutions is necessary for sustaining the environment and human health. The transfer of herbicides from agricultural systems to rivers and groundwater is of major concern for aquatic organisms and human health. Moreover, the herbicide residues may represent environmental risk and influence rotational crops [37]. Oxadiargyl, 5-tert-butyl-3-[2,4-dichloro-5-(prop-2-ynyl)oxy]phenyl]-1,3,4-oxadiazol-2(3H)-one, is a herbicide which is effective on grasses, broad-leaved weeds and annual sedges. It has been used primarily for weed control in rice and cane fields [38]. It degrades under anaerobic conditions and is dissipated rapidly into the sediment phase from water [39]. There are only a few works related to determination of oxadiargyl concentration in plant and aqueous samples [40,41] which were not sufficiently sensitive for the monitoring of oxadiargyl fate, especially along the last part of the monitoring plan [42].

The aim of this work is to develop SPME fibers on stainless steel wire as a mechanically stable and cheap alternative to existing methods of fiber preparation. The surface of the stainless steel was initially modified by (3-mercaptopropyl)trimethoxysilane (MPTS) and its surface was evaluated by energy dispersive X-ray (EDX) spectroscopy and cyclic voltammetry (CV). After modification, four different sol–gel fibers: polar and non-polar polydimethylsiloxane (PDMS), polyethylene glycol (PEG), and poly(ethylene propylene glycol) monobutyl ether (UCON) were applied to investigate their suitability for the determination of herbicide oxadiargyl in paddy water, lettuce, rice, and soil samples prior to gas chromatography–mass spectrometry analysis.

2. Experimental

2.1. Materials and chemicals

Oxadiargyl (99.0%) was purchased from Bayer (Monheim am Rhein, Germany). Methoxytrimethylsilane, hydroxyl terminated polydimethylsiloxane, poly(ethylene propylene–glycol) monobutyl ether (UCONHTF 14) and ethanol were purchased from Fluka (St. Gallen, Switzerland). Tetramethylorthosilicate (tetramethoxysilane), poly(methylhydrosiloxane) (PMHS), trifluoroacetic acid (TFA), polyethyleneglycol 400 (PEG 400), methylene chloride, methanol, sodium hydroxide, hydrochloric acid, ammonia, acetone and n-hexane were purchased from Merck (Darmstadt, Germany). Ultra pure water was used for preparation of blank and real samples (SG Wasseraufbereitung, Germany).

A stock solution of oxadiargyl (1000 mg L^{-1}) was prepared in methanol, and stored at 4°C . A series of standard solutions of oxadiargyl ($10\text{--}10,000 \text{ }\mu\text{g L}^{-1}$) was prepared weekly and stored in a refrigerator. The working standard solutions were prepared at various concentrations by diluting the stock solution as required in water and stored at 4°C . (3-mercaptopropyl)trimethoxysilane (95%) was purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. Instrumentation

SPME syringe was purchased from Supelco (Bellefonte, PA, USA). The SPME fiber assembly was prepared in our laboratory [43] and the proper fiber was assembled on it using a thermal resistant glue. A Yellowline TTS2 vortex mixer (Lennox, Ireland) and a Hettich universal 32R centrifuge (Hettich, Germany) were used to prepare sol solutions and separate precipitate from them. A Sonica 3300EP ultrasonic bath (SOLTEC, Milan, Italy) was used to prepare sol–gel and purify the materials.

An Agilent 6890N gas chromatograph (GC) equipped with a split/splitless injector, an Agilent 5975C mass selective detector

(MSD), and an Auto Sampler COMBI PAL (CTC analytics, Switzerland) were used. The mass spectrometer (MS) was operated in the electron ionization (EI) mode (70 eV). Helium (99.999%) was employed as a carrier gas and its flow rate was adjusted to 1 ml min^{-1} . The chromatographic separation was performed on a GC column HP5-MS ($30 \text{ m} \times 250 \text{ }\mu\text{m}$ ID and film thickness $0.25 \text{ }\mu\text{m}$) (J&W Scientific, USA). The initial temperature of the column was set at 60°C and held for 3 min, then increased by $40^\circ\text{C min}^{-1}$ to 180°C and maintained for 4 min, finally increased by $30^\circ\text{C min}^{-1}$ to 280°C and held for 2 min. The injector temperature was set at 275°C and desorption process was carried out in the splitless mode for 5 min. The temperature of GC–MS interface, ion source and quadrupole was set to 280, 230, and 150°C , respectively. The MS was operated in selected ion monitoring (SIM) mode at m/z of 213 and 178. The scanning electron microscopy (SEM) images and EDX spectrum were obtained by a TESCAN VEGA II XMU (Brno, Czech Republic). Cyclic voltammetry (CV) was performed using an Autolab model PGSTAT 20 potentiostat/galvanostat (Metrohm, The Netherlands).

2.3. Preparation of the MPTS self-assembled monolayers on stainless steel

Stainless steel wires were cleaned by sonication consecutively in ethanol, acetone and again in ethanol for 10 min in each, to remove any contaminants. The surface of the stainless steel wires were modified using MPTS. The film of the latter was formed on the surface of the stainless steel by dipping into a solution of 10^{-3} M of MPTS in ethanol for 3 h. After the formation of film, the surface was rinsed with ethanol, subsequently dried in a stream of argon and stored under argon atmosphere before characterization [44].

2.4. Cyclic voltammetry characterization

Cyclic voltammograms (CV) were acquired on bare as well as coated substrates. A three-electrode electrochemical cell with platinum wire and saturated calomel electrode (0.24 V vs. standard hydrogen electrode) as the counter and reference electrodes were used. CV measurements pursued to determine the efficiency of the chemisorption were carried out in 0.1 M NaOH electrolyte at a sweep rate of 10 mV s^{-1} in the potential window ranging from -0.6 to $+0.4 \text{ V}$. This potential range includes an anodic oxidation reaction, producing more chromium and iron oxidative products.

2.5. Energy dispersive X-ray (EDX) spectroscopy characterization

EDX spectra obtained for bare and modified stainless steel were compared to each other by elemental analysis of basic elements' (Fe, C, Cr, Ni, O, S, and Si) weight percentages.

2.6. Chemical modification of trimethoxy tail groups of the monolayer

Hydrolysis of the MPTS was carried out by immersion of the surfaces modified wires in 0.1 M HCl for 1 h. The MPTS-modified surfaces were then dipped for 10 min in water and dried in desiccator.

2.7. Preparation of SPME fibers

Four kinds of SPME fibers were employed: (1) polar and (2) non-polar poly(dimethylsiloxane) (PDMS), (3) UCON, and (4) polyethyleneglycol(PEG). They were prepared as reported previously [36] except that PEG 400 was used instead of PEG 4000. The surface characteristics of the sol–gel coated fibers were

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