



Contents lists available at ScienceDirect

Journal of Chromatography A

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



A sublimate sorbent for stir-bar sorptive extraction of aqueous endocrine disruptor pesticides for gas chromatography-electron capture detection

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ARTICLE INFO

Article history:

Received 23 February 2018
Received in revised form 4 June 2018
Accepted 5 June 2018
Available online xxx

Keywords:

Cyclododecane
Stir bar sorptive extraction
Sublimate sorbent
Endocrine disruptor pesticides

ABSTRACT

A dumbbell-shaped magnetic stir-bar with sublimate sorbent was prepared for the stir bar sorptive extraction (SBSE) of pesticides in an aqueous sample prior to gas chromatography-micro-electron capture detection (GC- μ ECD). Cyclododecane (CDD) was coated onto a magnetic stir-bar surface as a sublimate sorbent, and steel balls were placed on both ends to form a dumbbell-shaped magnetic stir-bar for SBSE. Four EDC pesticides including chlorpyrifos, ethion, bromopropylate, and λ -cyhalothrin in aqueous samples were selected as model species to examine the proposed SBSE and the following desorption.

The parameters studied were those affecting the extraction efficiencies including the coating (solvent for CDD and thickness), extraction (sample pH, stirring rate, time, and salting out effect), dissolution solvent volume, and the loss of CDD sublimated in air. The maximum extraction efficiency was obtained under the following conditions. The stir bar (with CDD thickness of 5.2 μ m) was added into a 10 mL sample solution (at pH 7) for a 20-min extraction at 600 rpm. Then, the stir bar was gently removed from the sample solution, disassembled, and immersed into a 0.2 mL insert tube consisting of 3 μ L hexane to dissolve; 1 μ L was used for GC-ECD analysis. The linear ranges were 0.005–5 μ g L⁻¹ with coefficients of determination ranging from 0.9950 - 0.9994. Detection limits (based on S/N = 3) of the four EDCs were 0.4–4.5 ng L⁻¹ with a relative standard deviation (RSD) of 2.4–6.3%, and quantitation limits (based on S/N = 5) were 1–15 ng L⁻¹. The relative recoveries of the spiked samples were in the range of 83.2–98.7% with RSDs of 2.1–8.4% in farm field waters. The proposed sublimation sorbent obtained excellent enrichment factors (101–834) and provided a simple, rapid, sensitive, and eco-friendly sample preparation method.

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1. Introduction

According to green chemistry, sample preparations that produce most of pollutants and spend the majority of operation time in chemical analysis have been studied with the aim of being environmental-friendly processes in recent decades [1,2]. Therefore, techniques to reduce the use of organic solvent, cost and extraction time, as well as increase detection sensitivity, have been investigated and developed [3–9]. Since the equilibrium extraction of solid-phase microextraction (SPME) was introduced [3], microextraction approaches including various liquid-liquid microextraction (LLME) have been developed to overcome the

shortcomings of traditional liquid-liquid extraction (LLE) to be a simple, rapid, and solvent-less technique for sample pretreatments [10–12].

SPME is based on the partitioning of analytes between the fiber sorbent phase and the aqueous sample matrix (or/and) its headspace [3,5]. The SPME sorbent is, however, typically only on the order of 0.5 μ L or less, the value of which limits the collecting quantity of analytes onto the fiber. Stir bar sorptive extraction (SBSE) was thus developed by coating a higher volume sorbent on the glass jacket that incorporated a magnetic stirring bar to increase the enriched factors [13–15]. Traditionally, stir bars are coated sorbents and are used to stir aqueous samples; thus, solutes are extracted and enriched into the sorbent layer. Similar to SPME, carryover may be a concern with the sorbent. Moreover, the friction loss of the coated sorbent and the analytes might occur also due to

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the direct contact with the bottom of the extraction vessel during stirring.

Cyclododecane (CDD) is a nonpolar lipophilic organic solid at room temperature with sublimation character [16]. Due to its relatively slow evaporation in comparison with other volatile binding mediums and its purity, it does not leave any residue after sublimation; CDD has been used on variety of materials, including paper, textile, ceramics and metals as a volatile temporary binding medium in conservation [16–19]. In this work, with the characters of high purity, sublimation and residue-less properties, the noble sublimate sorbent for SBSE was first proposed by using CDD coated on stir bar to solve the carryover problem [20–25]. Moreover, CDD has no electronegative element in its chemical structure; hence, it leaves no detection signals to interfere signals of analytes in GC-ECD. A dumbbell-shaped magnetic stir-bar was applied to prevent the friction loss of sorbent and extracted species [25–27]. In this study, a very convenient method was used to prepare an assembled dumbbell-shaped SBSE by using a small magnetic stir bar and two stainless balls. The dumbbell-shaped stir bar can be disassembled prior to desorption of analytical species to decrease the desorbed-solvent required.

Endocrine disrupting chemicals (EDCs) are compounds that alter the normal endocrine system of wildlife and humans [28–30]. A large number of pesticides have been identified as endocrine disruptors, such as chlorpyrifos, ethion, bromopropylate and λ -cyhalothrin, which were popularly used for orange fruits in Taiwan and are thus present in farm field waters at very low levels [31,32]. Therefore, a simple and sensitive method is needed for monitoring these compounds. The log octanol-water partition coefficients (Log Kow, at 20 °C) for chlorpyrifos, ethion, bromopropylate and λ -cyhalothrin are 4.77, 5.07, 5.43, and 5.99, respectively, which are not far from that of CDD (6.12). Therefore, they were selected as model species to examine the applicability of the proposed sublimate sorbent used for SBSE in aqueous samples.

In general, SBSE is accompanied with a thermal desorption chamber to desorb analytes wholly prior to gas chromatographic analysis [33,34]. Because solvent dissolution of the analytes with CDD sorbent was used instead of thermal desorption after the SBSE of four pesticides, the solvent for dissolution would be as small as possible to increase the fraction of extractant for GC- μ ECD analysis. Parameters affecting the coating of sublimate sorbent, the efficiency of SBSE and desorption were thoroughly investigated and optimized. The method was applied for the SBSE of four EDC pesticides in farm field water sample for GC- μ ECD analysis.

2. Experimental

2.1. Instrumentals and apparatus

An Agilent 6890 N (Wilmington, DE, USA) gas chromatograph (GC) equipped with a split/split-less injector and a micro-electron capture detector (μ ECD, 63Ni) was used in this work. The fused silica capillary column DB-608 (30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness) (Agilent Technologies, Palo Alto, CA, USA) was used to separate the four EDC pesticides. Nitrogen (99.999%) was used as both carrier gas and makeup gas at flow rates 1.0 and 50 mL min⁻¹, respectively. The GC was operated in split mode (purge 20 mL min⁻¹ after 4.5 min) with the injector temperature at 300 °C. The oven temperature was maintained at 150 °C for 1 min, and then, it was programmed at 6 °C min⁻¹ to 240 °C, where it was held for 1 min, and finally at 30 °C min⁻¹ to 280 °C, which was held for 4 min. The separated compounds were detected by μ ECD at 300 °C. Agilent Chemstation 4.01 software (Agilent Technologies) was used for instrument operation control and data analysis.

A Varian CP-3800 Gas Chromatograph / Varian Saturn 2200 GC/MS (Walnut Creek, CA, USA) was used to identify the analytes

with the same separation column eluting with He (99.9995%) at a flow rate of 1.0 mL min⁻¹ with the same temperature program described above. The temperatures of the ion source and transfer line were set at 200 °C and 280 °C, respectively.

A magnetic stirrer hotplate (Stirrer/Hotplate, Corning, USA) was used for SBSE. The microsyringe (10 μ L, 50 mm length, 0.63 mm O.D.) was from SGE (Trajan Scientific and Medical, Victoria, Australia). A 0.2 mL silanized insert tube (6 \times 31 mm) with wide opening, clear, conical, 15 mm tip, from MACHEREY-NAGEL GmbH (Duren, Germany) was used as the desorption vial.

2.2. Reagents and solutions

A TKA GenPure water purification system (Niederelbert, Germany) was used to produce ultrapure water (resistivity 18.2 M Ω \times cm, TOC 1–5 ppb) for preparations of all aqueous solutions. Chlorpyrifos (98.5%), bromopropylate (99%), and λ -cyhalothrin (98.5%) were from Dr. Ehrenstorfer (Augsburg, Germany), and ethion (99%) was from Riedel-de Haën (Seelze, Germany). Cyclododecane (99%) was from TCI (Tokyo, Japan). Methanol, ethanol, propanol, acetone and *n*-hexane (all HPLC grade), dipotassium hydrogen phosphate and sodium hydroxide (ACS grade) were from Merck (Darmstadt, Germany). Phosphoric acid (85%) was from Merck (Rockland, MA, USA). Nitrogen (99.999%) and helium (99.9995%) were obtained from the local supplier Lien-Hwa (Taichung, Taiwan).

Stock standard solutions of the four EDC pesticides (1000 μ g mL⁻¹) were prepared by dissolving 0.010 g of chlorpyrifos, ethion, bromopropylate and λ -cyhalothrin in 10 mL of methanol; stored in brown glass bottles with polytetrafluoroethylene (PTFE)-lined caps; and then kept in a 4 °C refrigerator. Working standards were prepared daily by diluting the stock standard solutions with methanol.

2.3. Preparation of the dumbbell-shaped sublimate sorbent for SBSE

The magnetic stir-bar (1-cm length with 2-mm diameter) and steel ball (6-mm diameter) were obtained from local suppliers (Taichung, Taiwan). CDD (0.5 g) was dissolved in 2 mL of solvent as dip-coating solution and kept in a 30 °C water-bath. The magnetic stir-bar was dipped into the CDD coating solution and taken out carefully to dry several times in a hood to build-up a sublimate sorbent. The dumbbell-shaped stir bar was assembled by placing steel balls onto both ends of the magnetic stir-bar pre-coated sublimate sorbent as demonstrated in Fig. 1(a).

SBSE should be achieved in sample solution as soon as the dumbbell-shaped stir bar device is assembled. After extraction, taking out the dumbbell-shaped stir bar carefully, and removal of both steel balls, the stir-bar was put into a 0.2 mL insert tube to dissolve sublimate sorbent and pesticides using 3 μ L hexane, and 1 μ L was injected for GC- μ ECD analysis. The operation process is presented in Fig. 1(b).

2.4. Sample collection and pretreatment using sublimate sorbent SBSE

Farm field water samples were collected from Dali, Taichung City. After filtrations by using 5B filter paper (5–10 μ m, 15 cm) (Advantec, Dublin, CA) and then a 0.22 μ m membrane filter (Toyo Roshi Kaisha, Tokyo, Japan), the sample solution was adjusted to pH 7.0 with phosphate buffer and kept in a 4 °C refrigerator. A dumbbell-shaped sublimate sorbent stir bar was freshly coated, assembled and then put into sample solution to achieve the SBSE.

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