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Determination of synthetic polycyclic musks in water by microwave-assisted headspace solid-phase microextraction and gas chromatography-mass spectrometry

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ABSTRACT

This paper describes a rapid and solvent-free method, microwave-assisted headspace solid-phase microextraction (MA-HS-SPME), for the extraction of six commonly used synthetic polycyclic musks: galaxolide (HHCB), tonalide (AHTN), celestolide (ADBI), traseolide (ATII), cashmeran (DPMI) and phantolide (AHMI) from water samples prior to their determination using gas chromatography-mass spectrometry (GC-MS). The effects of various extraction parameters for the quantitative extraction of these analytes by MA-HS-SPME were systematically investigated and optimized. The analytes in a 20-mL water sample (in a 40-mL sample-vial containing 4 g of NaCl) were efficiently extracted by a polydimethylsiloxane-divinylbenzene (PDMS-DVB) fiber placed in the headspace when the system was microwave irradiated at 180 W for less than 4 min. The limits of detection (LODs) ranged from 0.05 to 0.1 ng/L, and the limits of quantification (LOQs) were less than 0.2 ng/L. A preliminary analysis of wastewater samples revealed that HHCB and AHTN were the two most commonly detected synthetic polycyclic musks; using a standard addition method, their concentration were determined to range from 1.2 to 37.3 ng/L with relative standard deviation (RSD) ranging from 2 to 6%. The results obtained using this approach are better than those from the conventional oil-bath HS-SPME.

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1. Introduction

Synthetic musk fragrances comprise a group of chemicals used extensively in a number of consumer products (e.g., laundry detergents, fabric softeners, cleaning agents) and cosmetic and personal care products (e.g., perfumes, shampoos, body lotions, etc.). Because of their physical and chemical properties, these musks, much like other hydrophobic and semi-volatile organic pollutants, are found in various organisms including marine mammals in the food chain [1–3]. Synthetic polycyclic musks have been detected in various environmental samples worldwide, including air, freshwater, seawater, and sediments [4–8]. Because of their lipophilic properties, they have also been found in aquatic biota, such as mussels and fish, and even in human adipose tissue and breast milk [1,9–12]. The widespread use of synthetic polycyclic musks and increasing public concern stimulated our interest in developing a rapid and reliable method for determining their presence and fate in aquatic environments. Fig. 1 displays the structures and names of the six commonly used synthetic polycyclic musks [4–15] that were employed in the method development and validation of this study.

Many analytical methods have been developed to determine synthetic polycyclic musk residues in aqueous and solid samples. These approaches have been reviewed extensively by Peck [13], Pietrogrande and Basaglia [14], and Bester [15]. The extraction of these residues from water samples is commonly performed using liquid–liquid extraction (LLE) and solid-phase extraction (SPE). Recently, solid-phase microextraction (SPME) has been developed to replace these conventional methods to extract various musks from water samples because it is a relatively simple and solvent-free procedure [5]. Moreover, to avoid matrix effects and improve recovery, headspace solid-phase microextraction (HS-SPME) has also been developed to extract these analytes from aqueous samples [6]. For HS-SPME, heating the water sample increases the extraction efficiency; nevertheless, conventional heating from an external heat source (e.g., water- or oil-bath) is slow and poorly efficient. Microwave-assisted HS-SPME (MA-HS-SPME) has been developed recently as a simple, efficient, and rapid extraction process for the determination of various pesticides and semi-volatile pollutants from water and solid samples [16–18].

In this study, MA-HS-SPME coupled with GC-MS was employed to determine the presence of six synthetic polycyclic musks in aqueous samples. The effects of the SPME desorption conditions (temperature, time, and fiber depth in the GC injection-port) and extraction parameters (microwave irradiation power, irradiation time, sample-to-headspace ratio, and addition of NaCl) on

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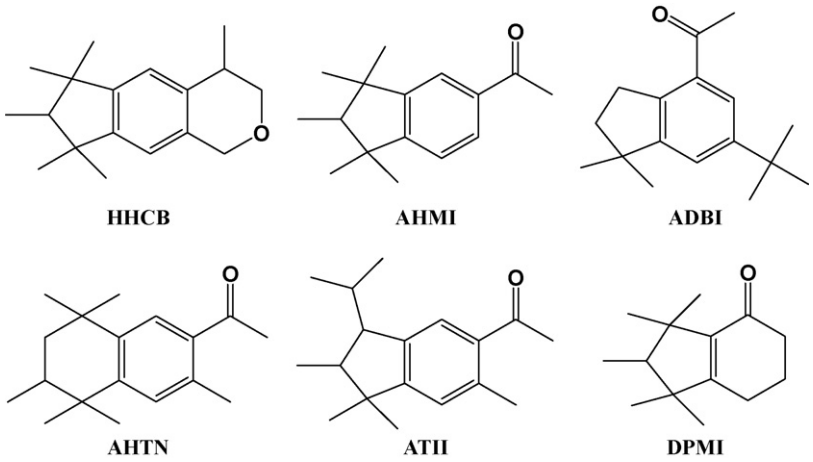

Fig. 1. Structures and names of the six commonly used synthetic polycyclic musks employed for method development and evaluation.

the quantitative extraction of these analytes using MA-HS-SPME were systematically investigated and optimized. The accuracy and precision of the method were evaluated and its effectiveness demonstrated for the determination of the six analytes in wastewater samples at trace-levels. Results were also obtained using conventional oil-bath HS-SPME for comparison.

2. Experimental

2.1. Chemicals and reagents

Unless stated otherwise, all chemicals and solvents were purchased in high purity grade from Aldrich (Milwaukee, USA), Tedia (Fairfield, USA) and Merck (Darmstadt, Germany) and used without further purification. The synthetic polycyclic musks: galaxolide (HHCB), tonalide (AHTN), celestolide (ADBI), traseolide (ATII), cashmeran (DPMI) and phantolide (AHMI) (purity > 97%) were purchased from LGC Promochem (Teddington, UK). Stock solutions of each analyte (500 μg/mL) were prepared in methanol. Mixtures of the analytes for the preparation of working standards were also prepared in methanol. All stock solutions and mixtures were stored in the dark at −4 °C.

2.2. Sample collection

Two wastewater samples were collected from (1) an outlet of a women's dormitory at National Central University, Taiwan (specific conductance: 440 μS/cm, pH 6.2), and (2) a ditch located 55 m downstream (specific conductance: 180 μS/cm, pH 6.8) from the outlet. A third water sample (specific conductance: 240 μS/cm, pH 6.6) was collected from a ditch located 100 m downstream from the industrial effluent outlet of a detergent manufacturer located in Taichung County (Taiwan). Upon arrival in the laboratory, the samples were adjusted to pH 2–3 through the addition of conc. HCl to depress microbial degradation, and then they were stored at −4 °C until required for analysis.

2.3. MA-HS-SPME

The set-up and procedure used for MA-HS-SPME have been described previously [16–18], and were performed with minor modifications. An SPME device consisting of a manual holder and a PDMS-DVB fiber was obtained from Supelco (Bellefonte, USA). The fibers were conditioned in the GC injection-port under nitrogen stream at a temperature 250 °C for at least 1 h prior to use. An aliquot of 20 mL water sample containing the six analytes was placed in a 40-mL sample-vial that was sealed with a screw cap featuring a PTFE-faced septum. For MA-HS-SPME procedure, the sample-vial was placed in a CEM Mars Xpress microwave system (Matthews, USA) equipped with a Teflon stand to hold the sample-vial. The SPME needle was inserted directly into the sample-vial through the hole at the top of the microwave system, and the fiber was exposed to the headspace over the water sample. A microwave leak detector (MD-2000, Less EMF, NY, USA) was used to ensure the safe operation of each experiment. For conventional oil-bath HS-SPME (OB-HS-SPME), the sample-vial was placed in a preheated oil-bath (90 °C) and the sample was extracted for 25 min (optimized). After extraction, the SPME device was immediately injected into the GC injection-port (depth: 4.0 cm) and desorbed at 270 °C for 2 min (optimized, see Section 3.2). To avoid carryover, the fiber was maintained in the GC injection-port with split mode for at least 7 min prior to performing the next experiment.

2.4. GC-MS analysis

Analyses were performed on a Finnigan Focus gas chromatograph coupled directly to a Focus DSQ quadrupole mass spectrometer (Thermo Finnigan, Waltham, USA) operated in selected ion monitoring (SIM) mode under electron-impact ionization (EI) for quantitation. The injection-port temperature was 270 °C in the splitless mode. A DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film, J&W, CA, USA) was used. The following GC temperature program was used: 50 °C for 4 min; a temperature ramp of 30 °C/min up to 170 °C; a temperature ramp of 1 °C/min up to 180 °C; a temperature ramp of 40 °C/min up to 300 °C; and then holding this temperature for 5 min (total analysis time: 26 min). The temperature of the transfer line was set at 275 °C; the ion source temperature was 200 °C. The dwell time was 100 ms/ion/scan, and the solvent delay was 5 min. The electron energy was 70 eV.

3. Results and discussion

3.1. GC-MS detection

As a first step, suitable gas chromatographic separation and stable mass spectra of these six synthetic polycyclic musks were obtained to provide the maximal detection sensitivity and specificity. These analytes exhibited some common fragmentation pathway. The molecular ions of these analytes were all detected with 20–50% intensities relative to their corresponding base peaks under electron-impact ionization. The base peak appeared at

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