Journal of Chromatography A, 1385 (2015) 12–19

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Monitoring of selected estrogen mimics in complicated samples using polymeric ionic liquid-based multiple monolithic fiber solid-phase microextraction combined with high-performance liquid chromatography

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ARTICLE INFO

Article history:
Received 4 December 2014
Received in revised form 22 January 2015
Accepted 23 January 2015
Available online 2 February 2015

Keywords:
Monolithic fiber solid-phase microextraction (MMF-SPME)
Polymeric ionic liquid
Estrogen mimics
Environmental water
Milk

ABSTRACT

A convenient, rapid, sensitive and environmentally friendly method for simultaneous monitoring of six estrogen mimics (bisphenol A, diethylstilbestrol, dienestrol, hexestrol, octylphenol and nonylphenol) in water and milk samples was developed by coupling multiple monolithic fiber solid-phase microextraction (MMF-SPME) to high performance liquid chromatography with diode array detection. The MMF-SPME based on polymeric ionic liquid-based monolith as extractive medium was used to concentrate target analytes. Because there were multiple interactions between adsorbent and analytes, the MMF-SPME exhibited a high extractive capability toward analytes. To obtain optimum extraction performance, several extraction parameters including desorption solvent, pH value and ionic strength in sample matrix, extraction and desorption time were investigated and discussed. Under the optimized extraction conditions, the limits of detection (S/N = 3) of the proposed method were 0.040–0.11 μg/L in water and in milk samples. Satisfactory linearity was achieved for analytes with the correlation coefficients (r) above 0.99. Excellent method reproducibility was achieved by evaluating the repeatability, intermediate precision and MMF-to-MMF reproducibility with relative standard deviations (RSDs) of both less than 10%. Finally, the proposed method was successfully applied to the determination of estrogen mimics in several milk and environmental water samples. Recoveries obtained for the determination of six target analytes in spiking samples ranged from 75.6% to 118%, with RSD below 10% in all cases.

1. Introduction

Estrogen mimics (EMs), such as bisphenol A (BPA), diethylstilbestrol (DES), dienestrol (DS), hexestrol (HS), octylphenol (OP) and nonylphenol (NP) are classified as potential endocrine disruptor chemicals and have attracted widespread attention in recent years [1–3]. The EMs can enter into the environment waters through all kinds of ways such as the excretion of human and animals, pharmaceutical wastewater and the aquaculture wastewater. At the same time, several studies have showed that some EMs residues were found in milk because of illegal application of EMs (such as DES, DS and HS) to promote growth rate of animals [4,5]. EMs can transport in blood and then are synthesized by the mammary glands and finally excreted in the milk. Studies have reported that EMs can mimic or block the actions of natural hormones in living organisms, including human, and impair their normal functioning, such as growth, metabolism and reproduction even at ultra-trace level [6,7]. Therefore, development of highly sensitive, rapid and accurate analytical method for monitoring of trace EMs in water and milk samples is necessary.

So far, gas chromatography (GC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) are the main analytical techniques for the determination of EMs. GC is rapid and sensitive, but derivatization step is needed in order to convert the analytes into more volatile derivatives [8,9]. The derivatization process is tedious and may cause the sample loss. CE possesses high separation performance, but it lacks stability and sensitivity for real samples with complicated matrices [10]. Compared with GC and CE, HPLC is simple and convenient. HPLC can analyze EMs directly without derivatization and exhibit good reproducibility

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http://dx.doi.org/10.1016/j.chroma.2015.01.072
0021-9673/

[11–14]. However, due to the very low levels of EMs and the complicated matrices in the real samples, sample pretreatment steps are required before the chromatographic analysis.

There are a few of sample pretreatment methods such as liquid–liquid extraction (LLE) [15,16], liquid phase microextraction (LPME) [17,18], hollow fiber liquid phase microextraction (HF-LPME) [11], solid phase extraction (SPE) [19,20] and stir bar sorptive extraction (SBSE) [21,22] that have been used to extract EMs from complicated samples. However, the LLE method demands time-consuming extraction and cleanup procedures, as well as large volumes of sample and toxic organic solvent. Multi-step processes including extraction, elution, evaporation and sample reconstitution steps are involved in SPE method. For SBSE, the friction between stir bar and the bottom of the vial during extraction can easily cause the loss of coating. At the same time, the extraction time is relatively long. The extraction capacity is limited for LPME and HF-LPME because low extractant is employed.

Solid phase microextraction (SPME), a solvent-free extraction method invented by Pawliszyn and co-workers in the 1990s, is another promising sample preparation technique [23,24]. SPME combines sampling and concentrating into a single step. At the same time, SPME has the merits of rapidness, convenience, easy-to-operate, low organic solvent consumption and environmental friendliness. As for the other extraction format, the extraction medium is the key in SPME; it determines the extraction targets and performance. At the same time, the sensitivity and precision of the analysis are also affected strongly by the extraction medium of SPME. So far, a number of materials have been prepared and used as the coating of SPME [25]. Typically, the thickness of coating is about dozens of micrometers, and the total volume of extraction medium is only at microlitre level. Therefore, the extraction capacity of SPME is limited. At the same time, the coatings of SPME may suffer from insufficient chemical/thermal stability during extraction. Up to now, coupled with GC [26–28] or HPLC [12,29–32], SPME has been successfully applied to the extraction and determination of several EMs from environmental samples. Pocurull et al. [32] used 85 μm polyacrylate coated fiber to extract estrogenic compounds from water samples. Expected extraction results were achieved, but the extraction equilibrium was long. For bisphenol A (BPA), it did not reach equilibrium and even the extraction time was prolonged to 60 min. The same circumstance also has been reported by Jiang et al. [33]. They used commercial 50 μm carbowax/templated resin (CW/TPR) coated fiber to extract BPA, 4-*n*-nonylphenol (NP), and 4-tert-octylphenol (OP) in environmental water samples. Results showed that the time of extraction equilibrium for BPA was 60 min. However, for NP and OP, the time was as long as 180 min. Therefore, to use SPME to extract EMs effectively and quickly, developing new extraction fibers is highly desired.

Multiple monolithic fiber SPME (MMF-SPME) with porous monolithic materials as extractive media is a new extraction format which was developed in our group [34,35]. Compared with conventional SPME fiber, there are several outstanding properties of MMF-SPME. Firstly, the MMF-SPME consisted of four independent substrateless thin monolithic fibers. Therefore, the total amount of extraction medium is higher than that of coated fiber, and high extraction capacity can be obtained. Secondly, the aqueous samples can form convection within MMF-SPME during extraction because there are gaps between thin fibers. The formation of convection favors the diffusion of analytes and accelerates the interaction between analytes and sorbent. Thus, MMF-SPME possesses quick extraction speed. Thirdly, the MMF-SPME uses porous monolithic materials as extraction media. Monoliths possess many intrinsic merits such as simple preparation, fast mass-transfer, varied chemical properties and so on. The extraction medium of MMF-SPME is very flexible. According to the character of target analytes, the monolithic fiber can be conveniently designed and prepared to realize effective extraction of analytes. In the present study, six EMs including bisphenol A, diethylstilbestrol, dienestrol, hexestrol, octylphenol and nonylphenol were selected as target analytes. A novel home-made MMF-SPME based on poly (1-allyl-3-methylimidazolium bis [(trifluoro methyl) sulfonyl] imide-*co*-ethylene dimethacrylate) (AMED) monolith was used to extract the target analytes. After optimization of the factors affecting the MMF/AMED-SPME of six target EMs (such as desorption solvent, extraction and desorption time, pH value and ionic strength in sample matrix), a combination of MMF/AMED-SPME with liquid desorption (LD), followed by high performance liquid chromatography with diode array detection (MMF/AMED-SPME-LD-HPLC/DAD) for the direct analysis of trace EMs in water and milk samples was developed.

2. Experimental

2.1. Chemicals

1-Allyl-3-methylimidazolium bis [(trifluoro methyl)sulfonyl]-imide (AM) (98%) was purchased from Cheng Jie Chemical Co., Ltd. (Shanghai, China); ethylene dimethacrylate (ED) (98%) was supplied by Alfa Aesar Ltd. (Tianjin, China); azobisisobutyronitrile (AIBN) (97%, recrystallized before use) and *N*,*N*-dimethylformamide (DMF) (98%), were purchased from Shanghai Chemical Co. (China); HPLC-grade acetonitrile (ACN) and methanol were purchased from Tedia Company (Fairfield, USA); water used throughout the study was purified using a Milli-Q water purification system (Millipore, USA).

BPA (99%) was purchased from TCI Co. (China), DES (99%), DS (98%) and HS (99%) were supplied by Sigma–Aldrich (Germany); OP (97%) and NP (96%) were purchased from Chemservice Co. (USA). The chemical properties of the above-mentioned analytes are shown in Table 1. Water samples were collected from Xiamen city and filtrated through 0.45 μm membranes. Different brands of milk were purchased from local retail markets. All samples were stored at −4 °C before use. Individual stock solutions of EMs were prepared at a concentration of 10.0 mg/L by dissolving methanol and renewed monthly. The standard mixtures of EMs were prepared by dissolving 2.00 mg of each compound in methanol in 100 mL volumetric flask. The stock solutions were stored at 4 °C and diluted with ultrapure water to give the required concentration.

2.2. Equipments and materials

HPLC analyses were carried out on Agilent 1260 LC chromatographic system (USA) equipped with a binary pump (1260 Quat Pump) and a diode array detector (1260-DAD). Sample injection was carried out using a RE3725i manual sample injector with a 20 μL loop (Rheodyne, Cotati, CA, USA), all experiments were performed at room temperature.

The MMF/AMED-SPME was prepared in our lab [35]. It consisted of four independent substrateless thin monolithic fibers (the dimension for each thin monolithic fiber was 20 mm in length and 0.5 mm in diameter). The chemical structure of the polymer monolithic material is displayed in Fig. 1.

2.3. Chromatographic conditions

The separation of six EMs was performed on a Hypersil BDS C18 column (5 μm particle size, 250 mm × 4.6 mm i.d.). Optimum separation was obtained with a binary mobile phase composed of ultrapure water (solvent A) and ACN (solvent B). The gradient elution program was as follows: 0.0–5.0 min = 55% B, 5.0–10.0 min = 55% B–100% B and kept to 12.0 min, 12.0–17.0 min = 100% B–55% B and