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Rapid determination of 54 pharmaceutical and personal care products in fish samples using microwave-assisted extraction—Hollow fiber—Liquid/solid phase microextraction

Yi Zhang[a,*], Wen Guo[a,b], Zhenfeng Yue[a], Li Lin[a], Fengjuan Zhao[a], Peijin Chen[a], Weidong Wu[a], Hong Zhu[b], Bo Yang[b], Yanyun Kuang[a], Jiong Wang[a]

[a] *Food Inspection and Quarantine Technology Center, Shenzhen Entry-Exit Inspection and Quarantine Bureau of China, Shenzhen, Guangdong, PR China*
[b] *School of Chemistry and Environment Engineering Shenzhen University, Shenzhen, Guangdong, PR China*

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ABSTRACT

In this paper, a simple, rapid, solvent-less and environmental friendliness microextraction method, microwave-assisted extraction-hollow fiber-liquid/solid phase microextraction (MAE-HF-L/SME), was developed for simultaneous extraction and enrichment of 54 trace hydrophilic/lipophilic pharmaceutical and personal care products (PPCPs) from fish samples. A solid-phase extraction material, solid-phase microextraction (SPME) fiber, was synthesized. The SPME fiber had a homogeneous, loose structure and good mechanical properties, and they exhibited a good adsorption capacity for most PPCPs selected. The material formed the basis for the method of MAE-HF-L/SME. A method of liquid chromatography-high resolution mass spectroscopy (LC–HRMS) for analysis of 54 PPCPs. Under optimal synthesis and extraction conditions, the limits of detection (LODs, $n = 3$) and the limits of quantitation (LOQs, $n = 10$) for the 54 PPCPs were between 0.01–0.50 $\mu g \cdot kg^{-1}$ and 0.05 2.00 $\mu g \cdot kg^{-1}$, respectively. Percent recoveries and the relative standard deviations (RSDs) in spiked fish samples ($n = 6$) were between 56.3%–119.9% and 0.3%–17.1%, respectively. The microextraction process of 54 PPCPs in MAE-HF-L/SME took approximately 12 min. The method has a low matrix interference and high enrichment factor and may be applicable for determination of 54 different PPCPs in fish samples.

1. Introduction

Pharmaceutical and personal care products (PPCPs) are an emerging genre of trace organic pollutants and include human and veterinary pharmaceuticals, disinfectants, healthcare products, etc. Daughton first identified the role of PPCPs as pollutants in 1999 [1]. Since then, PPCPs have been the topic of much research interest. In the environment, PPCPs are generally derived from hospitals and wastewater treatment plants [2–5]. These materials include unmetabolized drugs and personal care products that are discharged directly into the environment and sewage that is fed directly into rivers. Most PPCPs (and their metabolic products) have high polarities and high solubilities and are difficult to volatilize. Such species are difficult to remove from contaminated water. PPCPs are often detected at levels ranging from $ng\,L^{-1}$ to $\mu g\,L^{-1}$ worldwide in wastewater [6,7]. Many reports have documented the adverse eco-toxicological effects of some PPCPs even at trace levels [8–10]. PPCPs become enriched in organisms and gradually impacting human health [11,12].

The growing interest in measuring low concentrations of PPCPs in complex matrices has driven the development of many different extraction techniques. The first extraction techniques that were widely used included liquid-liquid extraction (LLE) [13,14] and solid phase extraction (SPE) [15,16]. However, the former technique requires high volumes of dangerous reagents and are laborious and time consuming [13,14,17], while the latter technique is difficult to operate and has a poor reproducibility and low recovery [18].

Hollow fiber-liquid phase microextraction (HF-LPME) was introduced by Pedersen-Bjergaard and Rasmussen [19], and it effectively prevents unwanted biological macromolecules from entering the extraction solvent, while reducing the level of matrix interferences compared to those observed in LLE. Hollow fibers are disposable, effectively preventing cross-contamination [20].

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* Corresponding author.
E-mail address: zhayi80@gmail.com (Y. Zhang).

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Because it requires little solvent, has a high purification efficiency, and is easy to operate, HF-LPME is a likely candidate for the determination of PPCPs. Zhao was the first to combine two modes of HF-LPME, static and dynamic HF-LPME, with gas chromatography-mass spectrometry (GC–MS) for the analysis of two polycyclic aromatic hydrocarbon (PAH) compounds in an aqueous sample [21]. They demonstrated the high enrichment and good reproducibility of these combined techniques. Dynamic hollow fiber-supported headspace liquid-phase microextraction (DHF-HS-LPME) combined with GC–MS was also used successfully for the quantitative analysis of PAHs in soil [22]. Sarafraz-Yazdi studied four triazole fungicides with HF-LPME/GC–MS and achieved a low limit of detection (LOD) of 0.3 μg/L–0.8 μg/L [23]. Solid-phase microextraction (SPME) is an emerging extraction technique that was developed after liquid phase and solid phase extraction. SPME has been used for the determination of several compounds [24–26]. For example, the selective determination of propranolol was achieved using SPME combined with in-tube molecularly imprinted polymer [27]. Kennedy used SPME/desorption electrospray ionization-mass spectrometry to analyze seven PPCPs in urine [28]. In SPME, sample injection, extraction, and concentration can occur at the same time, and its operation is simple, requires no solvent, has short analysis times, and is highly reproducible.

During LLE, analytes enter the extraction solution by adsorption or passive diffusion, leading to generally long equilibrium times. In SPME, binding sites in the stationary phase are easily occupied by disruptors, which confine the system to the complex matrix. LLE and SPME also share a common weakness; they have small extraction capacities, making it difficult to achieve the simultaneous extraction and enrichment of a variety of trace-level targets. Therefore, LLE with SPME were combined in this work to develop a simple extraction technology with a high enrichment factor (EF), a short equilibration time, and few matrix interferences.

In this paper, 54 representative targets were selected from seven types of PPCPs, including non-steroidal anti-inflammatory drugs (NSAIDs), sedatives, macrolide, sulfonamide, quinolones, other drugs, and a synthetic perfume [1,4,6,29,30]. The first six PPCP types were widely used human or animal drugs. NSAIDs have anti-inflammatory, analgesic, and antipyretic effects, while sulfonamide and quinolones have antimicrobial effects against gram-positive and some gram-negative bacteria. The wide use of these drugs has caused them to accumulate in the environment and damage human health. Some drugs in particular, such as mifepristone and bumetanide, have no clear classification, but their residues have been measured in the environment. Tonalide is widely used as a synthetic perfume. It was chosen for study because its potential risk to the environment and human health should also be considered.

In this work, an SPME fiber was synthesized with a high capacity, high concentration rate, stable performance, high efficiency, and low cost. This SPME fiber was then used for the determination of 54 PPCPs using microwave-assisted extraction-hollow fiber-liquid/solid phase microextraction (MAE-HF-L/SME). The synthetic SPME fiber is a good candidate for improving extraction processes by breaking the mass transfer balance of the HF-LPME process and allow targets in the organic phase adsorb on the SPME fiber's binding sites. In addition, the targets' extraction efficiency was dependent on the process of targets entered into organic phase from aqueous phase. By using microwave-assisted technology, the rate of targets diffusion was further improved to decrease the extraction time [31,32]. Overall, a method suitable for the simultaneous, rapid detection of 54 PPCPs was developed based on MAE-HF-L/SME combined with liquid chromatography-high resolution mass spectroscopy (LC-HRMS), and this approach was validated for the determination of PPCPs in fish samples.

2. Experimental

2.1. Materials

Mifepristone, praziquantel, acebutolol, phenformin, triprolidine, loperamide, naproxen, bumetanide, clopamide, cilnidipine, flumethasone, gliclazide, Cialis, vincristine, sulindac, itraconazole, and phenacetin were purchased from Sigma Aldrich (purity: 95%–99%, Sigma Aldrich Int., USA). Paracetamol, indometacin, ketoprofen, tonalide, carbamazepine, nadolol, dicyclomine, tramadol, lidocaine, clomipramine, amitriptyline, erythromycin, clindamycin, tylosin, tilmicosin, roxithromycin, sulfapyridine, sulfamethoxydiazine, sulfamerazine, brompheniramine, sulfamethoxazole, and sulfachinoxalin were acquired from Ehrenstorfer (purity: 95%–99%, Dr. Ehrenstorfer Int., Germany). Sulfamethoxypyridazine, sulfadimethoxine, sulfamonomethoxine, sulfadiazine, ormetoprin, trimethoprim, diaverdine, oxolinic acid, enrofloxacin, difloxacin, flumequine, ciprofloxacin lactate, nalidixic acid, pefloxacin, and enoxacin were purchased from WITEGA (purity: 95%–99%, WITEGA Int., Germany). Methacrylic acid (MAA), ethylene glycol dimethacrylate (EGDMA, Purity: 98%), styrene (ST), anhydrous ethanol, sodium chloride, and toluene were purchased from AR (AR, China). Azobisisobutyronitrile (AIBN) was purchased from CP (CP, China). Methanol, acetone, acetonitrile, and formic acid were purchased from Sigma Aldrich (HPLC grade, Sigma Aldrich Int., USA). High-purity water was prepared with a Milli-Q system (Millipore, Massachusetts, USA).

2.2. Instrumentation

A Q-Exactive mass spectrometer (Thermo Fisher Scientific Int., USA) with a C18 capillary column (150 mm × 2.1 mm i.d., 2.7 μm, Agilent, USA). A microwave synthesis/extraction workstation (MAS-II) was used for extraction. An oven (Binder, Germany) was used for the polymerization reaction. A vortex instrument (Thermo Fisher Scientific Int., USA) and a centrifuge (Sigma, USA) were used for sample preparation. A pressurized concentrator (TurboVap LU, Caliper Life Sciences, USA) was used to concentrate samples. An ultrasonic cleaner (E70H, Elmasonic, Germany) was used to clean samples. A hand-pressure sealing machine (FR-300L, Wanshida Welding Equipment Manufacturing Company, China) was used. Samples were stored in a culture dish. Both 25 μL and 50 μL capillary sample tubes were used (length: 125 mm, o.d.: 1.30 mm, ANPEL Scientific Instrument Co., Ltd, China). Polypropylene hollow fiber (i.d.: 1.2 mm, pore diameter: 0.2 μm, wall thickness: 200 μm) was obtained from Tianjin Polytechnic University. A disposable plastic film (Guangdong Home Bright Chemical Co., Ltd., China) was used to keep samples fresh. A 15 mL polyvinyl chloride pipe (Greiner Int., Germany) was used.

2.3. LC–HRMS conditions

For LC separations, analytes were first separated by gradient elution with a binary mobile phase composed of (A) 0.1% formic acid in water and (B) 0.1% formic acid in methanol. The column temperature was 30 °C, and the flow rate was 0.2 mL/min with a sample injection volume of 10 μL. The mobile phase gradient was established from 5% B to 50% B at 4 min, 80% B at 9 min, and then 95% B at 11 min. The gradient was maintained for 16 min, and column equilibration was completed at the initial condition for 4 min for a total run time of 20 min.

For HRMS measurements, the ion source was a heated electrospray ionization-II. The full MS scan mode for positive ion electrospray ionization was used at a spray voltage of 2.80 kV, a sheath gas flow rate of 35 arb, an auxiliary gas flow rate of 10 arb, a heater temperature of 320 °C, and a capillary temperature of 350 °C.