



Determination of 13 endocrine disrupting chemicals in sediments by gas chromatography–mass spectrometry using subcritical water extraction coupled with dispersed liquid–liquid microextraction and derivatization



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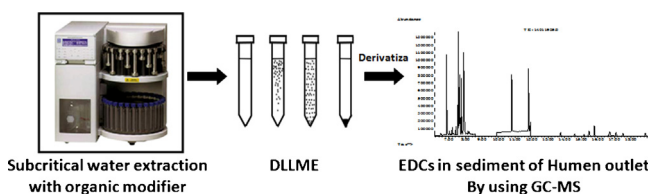
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HIGHLIGHTS

- We combine SWE with DLLME to determine EDCs in sediments using GC–MS with derivatization.
- Subcritical water was the extraction solvent for SWE and the sample solution for DLLME.
- Acetone was the organic modifier for SWE and the disperser solvent for DLLME.
- Parameters that affect the proposed method are optimized.
- We apply the optimal method to determine 13 EDCs in sediment of Humen outlet of the Pearl River.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a sample pretreatment method was developed for the determination of 13 endocrine disrupting chemicals (EDCs) in sediment samples based on the combination of subcritical water extraction (SWE) and dispersed liquid–liquid microextraction (DLLME). The subcritical water that provided by accelerated solvent extractor (ASE) was the sample solution (water) for the following DLLME and the soluble organic modifier that spiked in the subcritical water was also used as the disperser solvent for DLLME in succession. Thus, several important parameters that affected both SWE and DLLME were investigated, such as the extraction solvent for DLLME (chlorobenzene), extraction time for DLLME (30 s), selection of organic modifier for SWE (acetone), volume of organic modifier (10%) and extraction temperature for SWE (150 °C). In addition, good chromatographic behavior was achieved for GC–MS after derivatisation by using *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA). As a result, proposed method sensitive and reliable with the limits of detection (LODs) ranging from 0.006 ng g⁻¹ (BPA) to 0.639 ng g⁻¹ (19-norethisterone) and the relative standard deviations (RSDs) between 1.5% (E2) and 15.0% (DES). Moreover, the proposed method was compared with direct ASE extraction that reported previously, and

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the results showed that SWE–DLLME was more promising with recoveries ranging from 42.3% (dienestrol) to 131.3% (4,5 α -dihydrotestosterone), except for diethylstilbestrol (15.0%) and nonylphenols (29.8%). The proposed method was then successfully applied to determine 13 EDCs sediment of Humen outlet of the Pearl River, 12 of target compounds could be detected, and 10 could be quantitative analysis with the total concentration being 39.6 ng g⁻¹, and which indicated that the sediment of Humen outlet was heavily contaminated by EDCs.

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1. Introduction

Endocrine-disrupting chemicals (EDCs), which are defined by United States Environmental Protection Agency (U.S. EPA) as a diverse range of synthetic and natural xenobiotic that are able to disrupt or alter the functions of the endocrine system and consequently their adverse health effects in an intact organism [1], have been attracting increasing attentions [2–4].

EDCs in the environment were originated from excretion of human and animals, synthetic hormone drugs and industrial EDCs, they were widely distributed in various environmental matrix [5–7]. EDCs have relative high K_{OC} values as a series of hydrophobic organic compounds [8], they could be accumulated, biotransformed to more toxic metabolites and caused oxidative damages to aquatic organisms such as *crucian carp*. [9]. Therefore, in order to fully understand the fate of EDCs in the environment, especially in solid samples, a suitable determination method is highly desirable.

To date, a number of sample pretreatment methods have been developed for EDCs extraction from solid samples, such as extractive steam distillation [10], Soxhlet extraction [11], supercritical fluid extraction (SFE) [12], ultrasound-assisted extraction [13], microwave-assisted extraction [14] and accelerated solvent extraction (ASE) [15]. Moreover, ASE is believed to be the most efficient extraction procedure for simultaneous extraction and the only reliable extraction results and is easy to operate for automation [16]. Nevertheless, ASE can provide high temperature and high pressure simultaneously, subcritical water (water under high temperature and pressure, something in between liquid and solid) is therefore, introduced to ASE as extraction solvent [17]. Choosing water as extraction solvent can improve the selectivity for semi volatile organic pollutants which have relative high polarity such as EDCs, and adding organic modifier (soluble organic solvent) to subcritical water can improve enrichment factor.

Subcritical water extraction (SWE) offers many advantages compared to conventional organic solvent extractions. Subcritical water under high temperature can have a permittivity very similar to typical organic solvent, and this characteristic makes it possible to use water to selectively extract polar, midpolar, and nonpolar substances simply by changing its temperature and pressure [18,19]. So that SWE is proposed as an alternative greener processing method of traditional solvent extraction methods [20]. For example, enhanced recovery of total phenolics (TP) from defatted rice bran (DRB) subjected to prior microwave pretreatment was achieved by subcritical water extraction (SWE) [21]. However, analytes are diluted when transferred from solid into liquid by using SWE, and a lot of impurities could be co-extracted simultaneously. Thus, operations are needed to concentrate and purify the analytes from sample solution subsequently. Actually, hyphenated techniques have been introduced between SWE and solid phase extraction (SPE), solid phase microextraction (SPME) and hollow fiber microporous membrane liquid–liquid extraction for the determination of polycyclic aromatic hydrocarbons and chlorophenols in soil samples [22–24].

Dispersive liquid–liquid microextraction (DLLME) is a novel pretreatment method presented for liquid sample [25]. In this

method, analytes in water samples are extracted by a cloudy solution formed by an appropriate mixture of extraction solvent and dispersant, and then extraction solvent was separated by centrifugation. DLLME overmatched solid phase microextraction (SPME) and liquid phase microextraction (LPME) via its significantly larger mass transfer area and was convenient, rapid and sensitive [26,27]. Therefore, coupling DLLME with SWE was completely untapped for EDCs determination.

The aim of the present work was the development and validation of a pretreatment procedure using SWE coupled with DLLME. This study focused on taking advantage of the subcritical water and using water miscible organic solvents both as organic modifier for SWE and disperser solvent for DLLME. Some other key factors such as extraction solvent and time for DLLME, pH and organic modifier for subcritical water and ASE temperature were investigated as well. Moreover, the proposed method was then applied to evaluate the contamination of 13 EDCs in sediment sample that are collected from Humen outlet of the Pearl River.

2. Experimental

2.1. Chemicals and reagents

Nonylphenol, bisphenol A, dienestrol, *trans*-dehydroandrosterone, 4,5 α -dihydrotestosterone, β -estradiol, trenbolone, 19-norethindrone, 17 α -ethynylestradiol, 4-*n*-nonylphenol-d4, 17 α -ethynylestradiol-d4, estrone-d4 were purchased from Sigma–Aldrich (St. Louis, MO, USA). Hexestrol, diethylstilbestrol, androsterone, estrone and pyridine were purchased from Merck (Darmstadt, Germany). Ultra pure water was produced using Milli-Q Advantage A10 system (Bedford, MA, USA). Sodium hydroxide (NaOH), sodium chloride (NaCl), hydrochloric acid (HCl), and other reagents are of analytical grade supplied by Guangzhou chemical reagent factory. More information of the target analytes are listed in Table 1 including abbreviation, log K_{ow} values, CAS no. and molecular weight.

The individual stock solutions of 13 EDCs at 1.00 mg mL⁻¹ were prepared by dissolving 50 mg of each standard compound in 50 mL acetone with volumetric flask. A mixed stock solution of 20 μ g mL⁻¹ 13 EDCs was obtained by appropriate dilution of each stock solution with acetone. Dry ground soil was spiked by mix standard at the concentration of 80 ng g⁻¹, sufficient mixed and stood overnight before condition optimization. 4-*n*-nonylphenol-d4, 17 α -ethynylestradiol-d4 and estrone-d4, used as internal standard at the concentration of 80 ng g⁻¹.

2.2. Sample collection and preparation

The sampling site (22°48'35.9"N, 113°36'40.5"E) was located in the Humen estuary which was the largest one of the eight estuaries of the Pearl River of Guangdong province in China. Sediment samples were collected from Humen outlet and stored at -80 °C. After that, the collected sediments were freeze-dried and sieved to a grain size of <1 mm, homogenized and stored in the desiccators for method validation.

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