A highly sensitive and selective method for determination of phenoxy carboxylic acids from environmental water samples by dispersive solid-phase extraction coupled with ultra high performance liquid chromatography-tandem mass spectrometry

Zhongyin Ji[a,c], Jie Cheng[b], Cuihua Song[b], Na Hu[a], Wu Zhou[d], Yourui Suo[a], Zhiwei Sun[b,*], Jinmao You[a,b,c,**]

[a] Key Laboratory of Adaptation and Evolution of Plateau Biota, Northwest Institute of Plateau Biology, Chinese Academy of Science, Xining, PR China
[b] Key Laboratory of Pharmaceutical Intermediates and Analysis of Natural Medicine of Shandong Province, Qufu Normal University, Qufu, PR China
[c] University of Chinese Academy of Science, Beijing, PR China
[d] Qinghai University, Xining, PR China

ABSTRACT

A rapid and efficient method for extraction of 12 phenoxy carboxylic acids (PCAs) in environmental water samples was established based on metal–organic framework MIL-101 assisted dispersive solid phase extraction (DSPE). 12 PCAs were labeled by d_0-10-methyl-2-(piperazin-1-ylsulfonyl)anthracen-9(10H)-one(d_0-MASPz) and d_3-10-methyl-2-(piperazin-1-ylsulfonyl)anthracen-9(10H)-one(d_3-MASPz), allowing each analyte to have an isotope internal standard. A stable isotope-coded strategy for the detection of 12 PCAs was developed under optimized extraction conditions and UHPLC-MS/MS conditions. All PCAs analytes were in good linearity in the concentration range of 5–1000 ng/L, and the calibration function was verified by the Mandel fitting test with a 95% confidence level. The LODs and LOQs were estimated by the IUPAC's recommendations. The LODs ranged from 0.18 to 0.88 ng/L, and LOQs ranged from 0.59 to 2.90 ng/L. The intra-day and inter-day precision in three spiked levels (5, 50 and 100 ng/L) were in the range of (1.40 ± 0.14) %– (2.76 ± 0.12) % and (2.60 ± 0.26) %– (3.83 ± 0.32) %, respectively. The developed method has been successfully applied to the determination of PCAs in environmental water samples with recoveries ranging from 95.3% to 105.5%. All of the precision and recovery analyses were done in triplicate.

1. Introduction

Phenoxy carboxylic acids (PCAs) are a significant kind of herbicide which has been widely used in production due to their relative low cost, effectiveness, and less residual. However, in the past few decades, the existence of PCAs in environment has attracted attention because of toxicological risk of the contaminated water [1,2]. According to the low content of PCAs in the environment, most of the analytical methods previously published for the determination of these compounds are hard to satisfy the requirements of the detection of the trace PCAs. In the sight of that, a rapid, selective, and sensitive method for determining the trace levels of PCAs from environment samples is of great urgence and significant importance.

Several enriching methods have been developed in order to increase the detection sensitivity of PCAs, such as solid phase extraction (SPE) [3–5], magnetic solid phase extraction (MSPE) [6–8], solid phase microextraction (SPME) [9,10], liquid-liquid extraction (LLE) [11,12] and dispersive liquid–liquid microextraction (DLLME) [13]. However, as everyone knows, SPE is time consuming and tedious; LLE requires large amounts of organic solvents which are usually toxic and environmentally unfriendly; SPME is a solvent-free technique, but the fiber is expensive and fragile, and the problem of sample carry-over sometimes cannot be eliminated [14]. Therefore, in order to accurately determine the PCAs residues in the environment, dispersive solid-phase extraction combined with new materials has great potential in environmental analysis [15]. Metal organic framework materials (MOFs)

---

are a new nanoporous material similar to zeolite. Their unique characteristics make MOFs promising for diverse applications in analytical chemistry [16]. MIL-101 was used as an example of MOFs due to its attractive features as a sorbent for the extraction of pollutants in aqueous solution, such as high surface area, large pore windows, large pores, accessible coordinative unsaturated sites, and excellent chemical and solvent stability [17]. MIL-101 has been successfully explored as sorbents in enriching indole-3-acetic acid, indole-3-propionicacid, 1-naphthaleneaceticacid(1-NAA), 2,4,5-trichlorophenoxyaceticacid (2,4,5-T), et al. [14,18]. However, to the best of our knowledge, there is no report on the use for enriching PCAs via MIL-101.

High performance liquid chromatography coupled with various detectors is considered as the most suitable and common method for determination of PCAs. Several analytical methods were developed on HPLC-UV in the past [1,19]. However, HPLC-UV method was difficult to meet the demand for sample analysis due to its low sensitivity. The detection sensitivity could be improved greatly by the use of HPLC-FLD and derivatization via fluorescent reagents [14,20]. But HPLC-FLD methods need longer chromatographic run time in order to obtain better chromatography separation. UHPLC-MS/MS can shorten the run time and increase the analytical throughput by selective data acquisition [21–23]. Nevertheless, the detection sensitivity is still restricted because the PCAs are most easily ionized in negative mode as their conjugate base. In addition, matrix effects are also a major challenge to UHPLC-MS/MS analysis and isotope internal standards used to correct matrix effects are limited in variety and expensive.

In this work, a rapid, efficient and selective new method for enrichment of PCAs was developed based on MIL-101 assisted dispersive solid phase extraction with a filter. In this method, the ionic charge of excimer was reversed by the derivative reagent of acridine. The sensitivity of signal was enhanced, and the sensitivity of detection was further improved. At the same time, the matrix effect was overcome by isotope-coded derivatization and internal standard quantification. The method established in this work is fast, sensitive and accurate. It has a good prospect in the field of environment analysis.

2. Experimental section

2.1. Reagents and chemical

D0-MASPz and d3-MASPz were synthesized in our laboratory. Phenoxyacetic acid (PA), 3-Phenoxypropionic acid (PPA), 4-Phenoxybutyric acid (PB), 4-chlorophenoxyacetic acid (4-CPA), 2-methyl-4-chlorophenoxyacetic acid (MCPA), 3-(4-Chlorophenoxy)propionic acid (4-CPP), (2-methyl-4-chlorophenoxy) propionic acid (MCPP), 2, 4-dichlorophenoxyacetic acid (2, 4-D), dichlorprop (2, 4-DP), 2, 4-dichlorophenoxybutyric acid (2, 4-DB), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2-(2,4,5-trichlorophenoxy)propanoic acid (2,4,5-TP) were purchased from Sigma-Aldrich (Sigma-Aldrich Company, USA). Chemical structures of 12 PCAs were shown in Fig. 1 A.

10-methyl-acridone-2-sulfonyl chloride (MASC) was synthesized in our previous work [24]. Acetonitrile (HPLC grade) was purchased from Sigma-Aldrich (USA). Cr (NO$_3$)$_3$·9H$_2$O was purchased from Aladdin (Shanghai, China). 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC•HCl), ethyl alcohol (EtOH), N, N-dimethylformamide (DMF) and 4-dimethylaminopyridine (DMAP) were of analytical reagent grade (Shanghai Chemical Reagents, Shanghai, China). Four solvents used for optimization of extraction conditions, including methanol (MeOH), acetonitrile (MeCN), toluene and acetone, were all of analytical reagent grade. Pure distilled water was purchased from Watson (Guangzhou, China).

2.2. Apparatus

Experiments were performed using an Agilent 1290 series UHPLC system coupled with an Agilent 6460 Triple Quadrupole MS/MS system equipped with an Agilent Jet Stream electrospray ionization source (ESI source). System control, data acquisition and data processing were performed on Agilent Mass Hunter Workstation (version B.05.00). The synthesized MIL-101 was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD patterns were recorded with a Rigaku MiniFlex 600 diffractometer (Rigaku, Japan) using Cu K$_\alpha$ radiation (λ = 0.15418 nm) over the angular range from 5° to 80°. The morphology and microstructure of the samples were examined using a field emission scanning electron microscope (SEM, JSM 6700F, JEOL, Japan, at 5.0 kV). An ultrasonic cleaner (KQ2200E), a high-speed refrigerated centrifuge (TGL-16M) and a thermostat water bath (DF-2) were equipped for derivatization and DSPE experiments.

2.3. Synthesis of d0-MASPz and d3-MASPz

D0-MASC and d3-MASC [25] were used as raw materials for preparation of d0-MASPz and d3-MASPz. 200 mL of acetonitrile solution containing d0/d3-MASC (1 g) and 30 mL of aqueous piperazine solution (1 g) were successively added into a 250-mL flask, and then kept at 60 °C for 20 min. The reaction solution was then evaporated to dryness, washed with water, and filtrated. By applying these steps, a light yellow crystal of d0-MASPz or d3-MASPz was obtained. The crude products were recrystallized three times with EtOH (95%) to obtain a light yellow crystal with purity higher than 99%.

2.4. Synthesis of MIL-101

MIL-101 was synthesized according to [17] with a slight modification. Cr (NO$_3$)$_3$·9H$_2$O (4 g), terephthalic acid (1.64 g) and hydrofluoric acid (125 μL, 40 w/w %) were mixed with ultrapure water (70 mL). The obtained mixture was transferred to a Teflon-lined bomb. Then, the Teflon-lined bomb was sealed, placed in an oven, and left at 220 °C for 8 h. After cooling to room temperature, the reactants were filtered through the 250 mesh stainless steel filter screen to remove the residual terephthalic acid. Then the filtrate was moved to the 10 mL centrifuge tube, centrifuged and drained. The supernatant was washed with deionized water for 3 times. A green powder product was obtained after vacuum drying 24 h at 70 °C.

2.5. Preparation of Solutions

Individual stock solutions of the 12 PCAs (1.0×10^{-3} mol/L) were prepared in DMF, and the corresponding low concentrations of PCAs standard solutions were prepared by diluting the corresponding stock solutions with acetonitrile. The d0-MASPz and d3-MASPz solution (1.0×10^{-3} mol/L) was respectively prepared by dissolving 3.4 mg farinose solids in 10 mL acetonitrile. 0.12 g of DMAP was dissolved in 10 mL acetonitrile to obtain DMAP solution (1.0×10^{-2} mol/L). 0.1 g of EDC·HCl was dissolved in 10 mL acetonitrile to obtain EDC solution (5.0×10^{-2} mol/L). The solutions mentioned above were stored at 4 °C in a refrigerator.

2.6. Dispersive solid phase extraction

Sample preparation was carried out according to [26] with slight changes. Environmental water samples were acquired from two different rivers in Qufu. At first, 10 mg of MIL-101, added in 10 mL of environmental water samples, was ultrasonicated (100 W, 40 Hz) for