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RESEARCH PAPER

Analysis of Organophosphate Esters in Sediment Samples Using Gas Chromatography-Tandem Mass Spectrometry

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Abstract: An efficient extraction and purification method coupled to gas chromatography-tandem mass spectrometry (GC-MS/MS) with electron impact (EI) was developed to determine eight organophosphate esters (OPEs) in sediment samples. OPEs were extracted from the sediments through vortex oscillation for 1 min and ultrasonic extraction using 20 mL of *n*-hexane and acetone mixture (1:1, *V*/*V*) for 10 min, followed by purification by Florisil solid phase extraction (SPE) column and quantitative determination by GC-MS/MS. The result showed that this pretreatment method was simple and less solvent consumption. At three spiked levels of 10, 20 and 50 μg L^{-1}, the recovery of OPEs (except TEP) was between 80% and 120%, and the limits of detection for OPEs were 0.31 to 64.51 ng L^{-1}, showing a good precision and accuracy in the determination of OPEs in sediment.

Key Words: Organophosphate esters; Gas chromatography-tandem mass spectrometry; Sediment

1 Introduction

Organophosphate esters (OPEs) are the compounds whose hydrogen atoms of phosphoric acid are replaced by different hydrocarbon substituents, such as aryl, alkyl and chlorinated-alkyl. OPEs are widely used as additives in the products such as plastics, building materials, textiles, furniture and so on. In recent years, the production of OPEs have gradually increased in connection with their excellent flame retardant performance and the forbidden of polybrominated diphenyl ether in the world. As additive flame retardants, however, OPEs are easily released into the surrounding area and have been detected in various environmental media in many countries and regions[1–14]. Several studies showed that a variety of OPEs had biological toxicity, chlorinated OPEs, even carcinogenicity[7,15–17].

Extraction methods of OPEs from sediments were extensively studied, such as Soxhlet extraction[18], ultrasound-assisted extraction[1,19,20], microwave-assisted extraction[10,21], pressurized solvent extraction[11,14,22,23], etc. Although the traditional Soxhlet extraction is mature and stable, it requires large amount of organic solvent and time-consuming. van den Eede *et al*[24] found that ultrasonic extraction and Soxhlet extraction were effective with almost equivalent recoveries to target compounds. In view of the complex matrix of sediments, further clean-up of raw extracts is necessary before analysis. The common clean-up techniques are chromatographic column[11,23], gel permeation chromatographic column[10,14,22] and solid phase extraction (SPE)[12,20,23], etc. The advantages including simple operation, high degree of automation and favorable purification effect make the SPE be applied particularly widespread. The analytical methods for the determination of OPFRs are Gas chromatography (GC) with nitrogen-phosphorus detection (GC-NPD), GC-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS), etc. GC-NPD has high

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sensitivity to detect phosphorus compounds, but its stability is poor; GC-MS can generate abundant ion fragments, which maybe interfere with low quality ions through experience three McIntosh rearrangements. For LC-MS/MS, electrospray ionization source is subjected to the sample matrix interference, and maybe decrease the sensitivity. GC-tandem mass spectrometry (GC-MS/MS) has better applicability and reliability because its electron bombardment ionization source tolerates more matrix interference than the electrospray ionization source. Moreover, GC-MS/MS has a higher sensitivity than GC-MS when it works in the select reaction monitoring mode. In this study, OPEs were extracted from sediments by combination of eddy current oscillation and ultrasonic extraction, and the raw extracts were cleaned-up by Florisil cartridges and analyzed by GC-MS/MS. The satisfied results were achieved in this experiment.

2 Experimental

2.1 Instrument and reagent

The target analysis was performed on a TSQ-Quantum XLS gas chromatography-tandem mass spectrometer (Thermo Fisher). Extraction was carried out with Soxtec 2050 automatic Soxhlet system (FUSS). MTN-2800D nitrogen blowing (Huarui Boyuan) and SB-5200DTS Ultrasonic Cleaners (Xingzhi) were used for the sample treatment. SPE solid-phase extraction device (CNW), XW-8XA vortex generator (CNW), Millipore ultrapure water meter (Qilinbeier) and Florisil solid phase extraction cartridges (500 mg mL^{-1}, CNW) were also used in the experiment.

Ten OPEs standards included Tripropyl phosphate (TPrP) (purchased from Sigma-Aldrich), Triethyl phosphate (TEP), Tri-*n*-butyl phosphate (TnBP), Tri(2-chloroethyl) phosphate (TCEP), Tri(chloropropyl) phosphate (TCPP), Tri(dichloropropyl) phosphate (TDCP), Triphenyl phosphate (TPhP/TPP), Tri(2-ethylhexyl) phosphate (TEHP), Tri-*n*-butyl-d27-phosphate (TnBP-D27), and Triphenyl-D15-phosphate (TPhP-D15) (purchased from AccuStandard Company, America). Ethyl acetate, *n*-hexane, acetone, methylene chloride and methanol were all purchased from ANPEL Laboratory Technologies (Shanghai) Inc., China.

2.2 Sample pretreatment

Sediment samples were freeze-drying for 48 h, then grinded and sieved through 80 mesh sieve, stored at 4 °C.

2.2.1 Extraction

Sediment samples (2.0 g) were accurately weighed, then extracted with 20 mL mixed solvent of *n*-hexane and acetone (1:1, *V/V*), volatiled for 1 min, extracted by ultrasonic (temperature: 35 °C, frequency: 25 kHz, 2 min; 40 kHz, 2 min) for 10 min, and centrifuged for 10 min. The aforementioned extraction processes were repeated one more time after collection supernatant, and the twice supernatants were mixed and concentrated to about 1 mL, followed by an addition of appropriate amount activated copper (made sure that copper was not all sulfide) and 12 hours' standing for the further clean-up.

2.2.2 Clean-up

Florisil SPE cartridges were sequentially conditioned with 5 mL of methanol and *n*-hexane, then the raw extracts were loaded at a flow rate of 5 mL min^{-1} and the cartridges were washed with 3 mL of *n*-hexane, finally the cartridges were eluted with ethyl acetate. The final eluents were concentrated with a nitrogen evaporator, and then TPhP-D15 was added as internal standard for the further detection.

2.3 GC-MS/MS analysis

2.3.1 Conditions of chromatography system

A DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm) was used. High purity helium was used as carrier gas in constant current mode of 1 mL min^{-1}. The injection-port temperature was set at 280 °C and the injection volume was 1 μL in the splitless mode. The following GC temperature program was as follows: 50 °C for 1 min; a temperature ramp of 25 °C min^{-1} up to 200 °C (holding this temperature for 1 min); a temperature ramp of 2 °C min^{-1} up to 210 °C (holding this temperature for 1 min); a temperature ramp of 25 °C min^{-1} up to 250 °C (holding this temperature for 1 min); a ramp of 2 °C min^{-1} up to 260 °C; a temperature ramp of 25 °C min^{-1} up to 300 °C (holding this temperature for 2 min).

2.3.2 Condition of mass spectrometry

The temperatures of ion source and transfer line were 250 °C and 280 °C, respectively. Selected reaction monitoring mode (SRM) was chosen, high purity argon gas was used as collision gas, and impact pressure was 0.133 Pa.

3 Results and discussion

3.1 Optimization of GC-MS/MS conditions

The mixed standard (1 μg mL^{-1}, including 8 kinds of targets, TPrP-D15 and TnBP-D27) was separated by baseline under the optimal conditions. In full scan mode, characteristic ion of each target was picked up, and then imposed 10–50 eV of collision energy to parent ions respectively for ion-scanning and the preliminary optimization of collision energy would be obtained. On the basis of the preliminary optimization, the