# Microwave-assisted headspace solid-phase microextraction for the rapid determination of organophosphate esters in aqueous samples by gas chromatography-mass spectrometry

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## ABSTRACT

The rapid and solvent-free determination of organophosphate esters (OPEs) in aqueous samples via one-step microwave-assisted headspace solid-phase microextraction (MA-HS-SPME) followed by gas chromatography–mass spectrometry (GC–MS) analysis is described. Tri-n-butyl phosphate (TnBP) and tris-(2-ethylhexyl) phosphate (TEHP) were selected as model compounds for the method of development and validation. The effects of various extraction parameters for the quantitative extraction of these analytes by MA-HS-SPME were systematically investigated and optimized. The analytes, in a 20 mL water sample (in a 40 mL sample bottle containing 2 g of NaCl, pH 3.0), were efficiently extracted by a polydimethylsiloxane-divinylbenzene (PDMS-DVB) fiber placed in the headspace when the system was microwave irradiated at 140 W for 5 min. The limits of quantification (LOQs) for TnBP and TEHP were 0.5 and 4 ng/L, respectively. Using the standard addition method, MA-HS-SPME coupled with GC–MS was utilized to determine selected OPEs in surface water and wastewater treatment plants (WWTP) influent/effluent samples. Preliminary results show that TnBP was commonly detected OPEs in these aqueous samples, the correlation coefficients ($r^2$) of the standard addition curves were greater than 0.9822, indicating that the developed method appears to be a good alternative technique for analyzing OPEs in aqueous samples.

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## 1. Introduction

Organophosphate esters (OPEs) are used widely as additives in flame retardants and plasticizers in a large variety of materials including polyurethane foams, PVC plastics, wall papers, paints, textiles, and electronic equipments. Although OPEs are generally considered to be less toxic and harmful than the brominated flame retardants (BFRs), triphenyl phosphate (TPhP) and tri-n-butyl phosphate (TnBP) have been reported to have neurotoxic properties [1,2]. OPEs are more water-soluble than the brominated flame retardants (e.g., PBDEs or HBCDs), and have been detected worldwide in a wide variety of environmental samples including wastewater, surface water, indoor air and dust [3–11], and even in human urine [12].

A number of analytical methods have been developed to determine OPEs in aqueous and solid samples, and have been reviewed extensively by Quintana et al. [13]. The extraction of these compounds from aqueous media is commonly achieved by liquid–liquid extraction (LLE) and solid-phase extraction (SPE) [3–5,13]. Solid-phase microextraction (SPME) has been recently developed to replace these conventional methods for extracting various organophosphate esters flame retardants (OPFRs) from water samples because it is relatively a simple and solvent-free procedure [6]. To avoid matrix effects, headspace solid-phase microextraction (HS-SPME) has also been developed for the extraction of volatile and semi-volatile analytes from aqueous samples, and even with high boiling point compounds, such as 5 and 6-ring polycyclic aromatics hydrocarbons (PAHs) [14,15]. To increase extraction efficiency, heating the aqueous sample has been suggested; nevertheless, conventional heating from an external heat source (e.g., water- or oil-bath) is slow and inefficient. Microwave-assisted HS-SPME (MA-HS-SPME) has recently been developed as a simple, efficient, and rapid extraction process for the determination of various pesticides and semi-volatile pollutants (i.e., PAHs, polychlorinated biphenyl, synthetic polycyclic musks) from water and solid samples [16–21].

In this study, rapid MA-HS-SPME coupled with GC–MS was employed to quantitatively determine OPEs in aqueous samples. The effects of the extraction parameters (microwave irradiation power, irradiation time, addition of NaCl, pH value and sample-to-headspace ratio) on the quantitative extraction of these analytes

**Table 1**
Detection characteristics, linear range, linearity, and limits of detection and quantitation.

| Analyte | Retention time (min) | (EI)MS–SIM–quantitation ions ($m/z$)[a] | Linear range (pg/mL) | $r^2$ | LOD (ng/L) | LOQ (ng/L) |
|---|---|---|---|---|---|---|
| TnBP | 6.86 | **99 ($[H_4PO_4]^+$)**, 151 ($[M-C_4H_8)]^+$) 211 ($[M-(C_4H_8)_2]^+$) | 5–100 | 0.9974 | 0.2 | 0.5 |
| TEHP | 9.80 | **99 ($[H_4PO_4]^+$)**, 113 ($[C_8H_{17}]^+$) | 10–200 | 0.9992 | 1.5 | 4 |

[a] Ions in bold are the base peaks in EI mass spectra.

using MA-HS-SPME were systematically investigated and the results are reported herein. The accuracy and precision of the method were evaluated, and its effectiveness in determining the selected OPEs in surface and wastewater samples at trace-levels was also examined. Tri-n-butyl phosphate and tris-(2-ethylhexyl) phosphate (TEHP), the two commonly detected OPEs in various environmental samples [3–11], were employed in the method of development and validation in this study.

## 2. Experimental

### 2.1. Chemicals and reagents

Unless stated, all high-purity chemicals and solvents were purchased from Aldrich (Milwaukee, WI, USA), Mallinckrodt Baker (Phillipsburg, NJ, USA) and Merck (Darmstadt, Germany), and were used without further purification. Standards TnBP and TEHP (purities ≥99%) were purchased from Aldrich. Stock solutions of each analyte (0.5 mg/mL) were prepared in ethyl acetate. Mixtures of the analytes for standard preparation and sample fortification were prepared in ethyl acetate. Deionized water was further purified using a Millipore water purification device (Billerica, MA, USA).

### 2.2. Sample collection

Two surface water samples were collected from: (1) a ditch located 55 m downstream from the outlet of a dormitory at National Central University, (2) a ditch located 100 m downstream from the outlet of a medium-size electric parts manufacturer located in Taoyuan County, Taiwan. The WWTP influent and effluent samples were collected from the An-Ping community in Tainan city. This WWTP performs mechanical clarification and flocculation filtration (population equivalent: 380,000). All samples were collected in duplicate (500 mL for each) and shipped to the laboratory in ice-packed containers. On arrival, the samples were immediately passed through a 0.45 μm membrane filter (Advantec MFS, CA, USA), adjusted to pH 3.0 by adding conc. hydrochloric acid to depress microbial degradation, stored at 4 °C, and analyzed in 1 week.

To eliminate contamination, all glassware was soaked in a solution of 5% (w/w) sodium hydroxide in ethanol for at least 12 h, and then cleaned and subsequently rinsed with deionized water, ethanol and acetone before drying, followed by overnight heating at 250 °C. After performing this procedure, no chemical background of target compounds was detected by GC–MS analysis as described below.

### 2.3. MA-HS-SPME

The set-up and procedure used for MA-HS-SPME has been described previously [20,21], and was performed with minor modifications. An SPME device consisting of a manual holder and a PDMS-DVB (65 μm) fiber was obtained from Supelco (Sigma–Aldrich, St. Louis, MO, USA). The PDMS-DVB fiber has proved the best recovery for the extraction of OPEs from the water samples [6]. The fibers were conditioned in the GC injection-port under a stream of nitrogen at a temperature 250 °C for at least 1 h prior to use. A 20 mL aliquot of water sample containing the two

analytes was placed in a 40 mL sample bottle, 3 g of sodium chloride was added to the bottle and the pH was adjusted to 3.0 by adding conc. hydrochloric acid (optimized, see Section 3.1). The sample bottle was then sealed with a screw cap featuring a PTFE-faced septum. For the MA-HS-SPME procedure, the sample bottle was placed in a CEM Mars Xpress microwave system (Matthews, NC, USA) equipped with a teflon stand to hold the sample bottle. The SPME needle was inserted directly into the sample bottle through the hole at the top of the microwave system, and the fiber exposed to the headspace over the water sample. A microwave leak detector (MD-2000, Less EMF, NY, USA) was used to ensure the safe operation of each experiment. After extraction, the SPME device was immediately injected into the GC injection-port and desorbed at 250 °C for 3 min. To avoid carryover, the fiber was maintained in the GC injection-port with the split mode for at least 5 min prior to perform the next experiment.

### 2.4. GC–MS analysis

Analyses were performed on a Finnigan Focus gas chromatograph coupled directly to a Focus DSQ quadrupole mass spectrometer (Thermo Finnigan, Waltham, USA) operated in the selected ion monitoring (SIM) mode under electron-impact ionization (EI) for quantitation. The injection-port temperature was 250 °C in the splitless mode. A DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film, J&W, CA, USA) was used for the separation. The following GC temperature program was used: 75 °C for 2 min; a temperature ramp of 30 °C/min up to 215 °C; a temperature ramp of 25 °C/min up to 300 °C; then hold at this temperature for 1 min (total analysis time: 11 min). The temperature of the transfer line was set at 275 °C; the ion source temperature was 200 °C. The dwell time was 100 ms/ion/scan, and the solvent delay was 5 min. The electron energy was 70 eV. Table 1 presents an overview of the retention times and two or three major ions used as quantitation ions for the GC–MS–SIM analysis. These quantitation ions correspond to the protonated phosphoric acid ($m/z$ 99, as the base peak) attributed to have undergone three consecutive McLafferty rearrangements, and the characteristic ions of $[M-(C_4H_8)_n]^+$ for TnBP, and $[C_8H_{17}]^+$ for TEHP [22].

## 3. Results and discussion

### 3.1. Optimization of one-step MA-HS-SPME

The microwave irradiation power and irradiation time are two important parameters that effect extraction efficiency of the MA-HS-SPME technique. A 20 mL water sample (spiked final concentration: 20 ng/L) was placed in a 40 mL sample bottle for each evaluation process. The procedure consisted of an experimental plan involving 16 runs to evaluate optimal irradiation power and irradiation time simultaneously (Table 2). Fig. 1 shows the normalized peak intensities (referred to as "recovery from the spiked samples") when the irradiation power was increased from 140 to 200 W, and when the irradiation time was increased from 2 to 5 min, respectively. This figure demonstrates the effect of the extraction temperature (referred to as "irradiation power") and extraction time on the MA-HS-SPME efficiency of the analytes. The maximum extraction efficiency was reached when the irradiation