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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.

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

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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

Table 2
Experimental plan for the microwave irradiation power and irradiation time of MA-HS-SPME.

Run	Irradiation power (W)	Irradiation time (min)
1	140	2
2		3
3		4
4		5
5		6
6	160	3
7		4
8		5
9	180	2
10		3
11		4
12		5
13	200	2
14		3
15		4
16		5

power and time was 140 W and 5 min, respectively. However, at higher irradiation powers, the water sample boiled and the recovery decreased presumably because of the decrease in the partition coefficient between the fiber coating and the headspace at higher temperatures [18–20].

In most cases, adjusting the pH value and the addition of a salt for aqueous samples are required to enhance the extraction efficiency by SPME [17,23,24]. Fig. 2(a and b) shows that the normalized peak intensities increased upon increasing pH from 1 to 3, especially for TnBP, and the peak intensities increased upon increasing the NaCl addition up to 2 g, then decreased gradually when 4 g of NaCl was added. These phenomenon may indicate that the acidified sample and the rising salt content increased the salting-out effect during the microwave irradiation and, therefore, affect the partitioning between the headspace and the analytes, however, when the salt content was too high, the viscosity of the sample increased leading to lower extractability.

The volume of the headspace is another factor that can affect extraction efficiency [18,19,24,25]. Here, the effect of the sample-to-headspace ratio was evaluated at an irradiation power of 140 W and an irradiation time of 5 min. A 40 mL sample bottle was chosen for this study because it was compatible with the size of the hole at the top of the microwave system. Various volumes of water sample (spiked final concentration: 20 ng/L) were placed in the bottle to obtain an adequate ratio and maximum peak intensity.

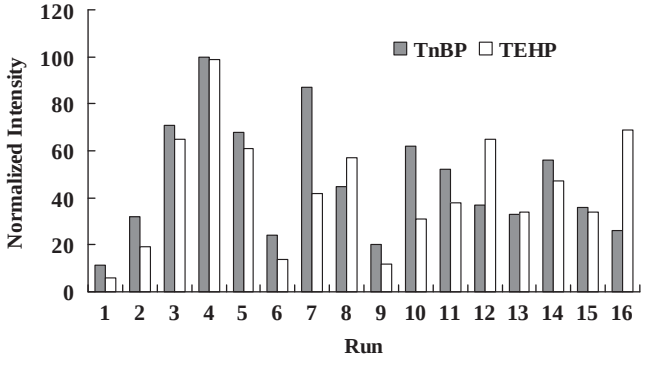

Fig. 1. Simultaneous effects of microwave irradiation power and irradiation time on the related peak intensity obtained using the MA-HS-SPME technique. The procedure consisted of an experimental plan involving 16 runs that are listed in Table 2. The data were normalized to the maximum peak area obtained in each set of experimental conditions.

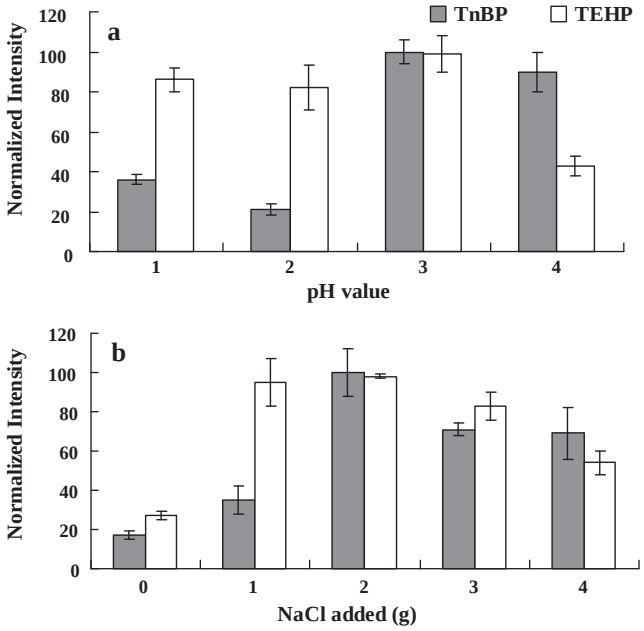

Fig. 2. Effects of (a) pH and (b) the addition of NaCl on peak intensities obtained using the MA-HS-SPME technique. Three replicate experiments were performed; the error bars represent standard deviations. The data were normalized to the maximum peak area obtained in each set of experimental conditions.

The best extraction efficiency occurred at a sample-to-headspace ratio of 1:1 (data not shown). Although a larger sample volume might increase the total extent of extraction of analytes by the fiber, when the volume was increased to 30 mL the fiber was situated impractically close to the surface of the water sample; in such experiments, droplets were observed on the fiber, causing lower recoveries through interference in the partitioning of the analytes between the fiber and the headspace. Collectively, these results indicate that the optimal conditions for extracting two selected OPEs from water samples by MA-HS-SPME were an irradiation power of 140 W, an irradiation time of 5 min, a pH value adjusted to 3, 2 g NaCl added to the sample, and a sample-to-headspace ratio of 1:1.

3.2. Method performance and applications

The analytical characteristics of the optimized MA-HS-SPME method in terms of its linear response range, reproducibility, limits

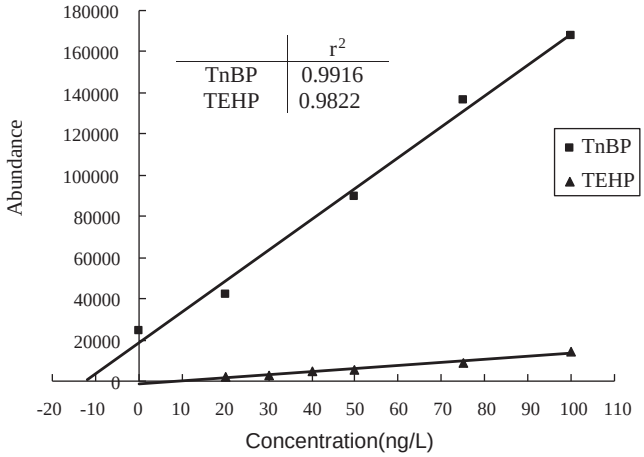

Fig. 3. Standard addition curves for the two analytes in the effluent-I sample obtained from the An-Ping WWTP.

of detection (LODs) and limits of quantitation were investigated, in order to estimate the efficiency and the feasibility for application to the analysis of environmental samples. Table 1 reveals that excellent linearities (correlation coefficient (r^2) greater than 0.9974) existed in the five-level calibration curve in the range from 5 to 100 ng/L for TnBP and 10 to 200 ng/L for TEPH. The LODs, defined at a signal/noise (S/N) ratio of 3, were determined through MA-HS-SPME analyses of spiked surface water sample-1; the values were 0.2 and 1.5 ng/L for TnBP and TEHP in 20 mL water samples, respectively. The LOQs, defined as concentrations required for S/N ratios of 10, were 0.5 and 4 ng/L, respectively. These data reveal that the combination of MA-HS-SPME and GC–MS–SIM ensures high reproducibility with excellent linearity and sensitivity for the analysis of these OPEs. Next, to compensate the matrix effect of the real environmental samples, the developed method was employed in conjunction with the standard addition method to quantitate the concentrations of TnBP and TEHP in two surface water samples and WWTP influent/effluent samples. Five bottles, each containing 20 mL of a water sample, were spiked with standard analyte solutions to obtain final concentrations of 0, 20, 50, 75 and 100 ng/L, respectively. Fig. 3 displays standard addition curves for the two analytes in the effluent-I sample obtained from the An-Ping WWTP. Table 3 lists the spiked recoveries and the concentrations of TnBP and TEHP detected in these aqueous samples and the correlation coefficients (r^2) of the standard addition curves. Fig. 4 displays the GC–(EI)MS–SIM chromatograms of (a) the standards, (b) the non-spiked and (c) the spiked effluent-I samples obtained from the An-Ping WWTP. The recoveries of these analytes from spiked deionized water and the real aqueous samples ranged from 86 to 106%. Preliminary results show that TnBP was commonly detected OPE in these aqueous samples, with concentrations ranging from 1.5 to 69 ng/L. The correlation coefficients (r^2) of the standard addition curves were all greater than 0.9822, indicating that the accuracy and repeatability of this developed MA-HS-SPME method is acceptable. Thus, the developed method appears to be an appropriate technique for analyzing selected OPEs in aqueous samples.

Comparison with previous studies listed in Table 4 reveals that the extraction time for MA-HS-SPME was 5 min, traditional liquid–liquid extraction required at least 20 min [4], and solid-phase extraction required 60–90 min (depending on the SPE flow rate, sample volume and SPE manifold set-up) [3,6]. No solvent consumption occurred in the case of MA-HS-SPME, but for LLE and SPE the value was more than 20 mL [3–6,26]. Moreover, comparisons with the extraction time for other microextraction methods, direct immersion-SPME required 40 min [6], membrane-assisted solvent extraction 3 h [8], and microwave digestion coupled with SPME 40 min [27]. The LOQs achieved by our present method are lower than those obtained using other methods, and the recoveries of the spiked samples are not significantly different. Furthermore, MA-HS-SPME proved to work well in detecting TEHP, which has made difficult to detect in previous reports due to its lipophilic character [6,28].

Table 3
Spiked recovery (%) and concentrations (ng/L) of two OPEs detected in various aquatic samples using the optimized MA-HS-SPME.

Sample	Analytes	
	TnBP	TEHP
Deionized water spiked recovery	89%[a] (12)[b]	106%[a] (6)[b]
Surface water-1	1.5[c] (15)[d]	nd
r^2	0.9902	0.9861
Surface water-2	35 (15)	nd
r^2	0.9872	0.9943
Spiked recovery	90%[a] (7)[b]	99%[a] (9)[b]
WWTP-influent	69 (8)	nd
r^2	0.9948	0.9961
WWTP-effluent-I	12 (14)	nd
r^2	0.9916	0.9822
Spiked recovery	86%[a] (5)[b]	88%[a] (7)[b]
WWTP-effluent-II	21	nd
r^2	0.9923	0.9873
WWTP-effluent-III	18	nd
r^2	0.9892	0.9885

r^2: the correlation coefficients of the method of standard addition curves.n.d.: not detected at the LOQ listed in Table 1.
[a] Mean spiked recovery ($n = 3$) at final concentration of 20 ng/L for each analytes.
[b] Relative standard deviation (% RSD) of spiked recovery is given in parentheses($n = 3$).
[c] Mean concentration (ng/L, $n = 3$) of selected OPFRs found in water samples.
[d] Relative standard deviation (% RSD) of detected concentration is given in parentheses ($n = 3$).

Table 4
Comparison of our method with previous studies.

Matrix	Extraction method	Detection	Recovery	Precision	LOD/LOQ/MQL	Ref
Surface water, influent/effluent	MA-HS-SPME (5 min)	GC–MS–SIM	TnBP: 86–90% TEHP: 88–106%	TnBP: 8–15% TEHP: 6–9%	LOD: TnBP: 0.2 ng/L, TEHP: 1.5 ng/L; LOQ: 0.5 ng/L, 4 ng/L	This study
WWTP effluents	Oasis HLB-SPE (>60 min)	LC–ESI–MS/MS	TnBP: 65–90% TEHP: 50–70%	TnBP: 1–11% TEHP: 1–16%	LOQ: TnBP: 20 ng/L, TEHP: 38 ng/L	3
STP effluents	LLE (165 mL DCM)	GC–NPD	Variations upto 59%	N.A.	LOD: 0.8–2.9 ng/L	4
WWTP effluents	LLE (25 mL DCM)	LC–ESI–MS/MS	80–94%	1.9–12%	MQL: TnBP: 11 ng/L, TEHP: 7.2 ng/L	5
Various water samples	Direct SPME (40 min at room temp.)	GC–NPD	TnBP: 107.0 ± 5.7% TEHP: 26.7 ± 17.3%	TnBP: 5–7% TEHP: 17–35%	LOQ: TnBP: 0.01 μg/L, TEHP: N.A.	6
Influent/effluent	MASE (3 h)	LC–ESI–MS/MS	TnBP: 100–112%	TnBP: 2–13%	LOQ: TnBP: 3 ng/L	8
Surface water	Stirring toluene (10 mL, 30 min)	GC–MS–SIM	TnBP: 98%	TnBP: 19%	LOD: TnBP: 10 ng/L	26
Wastewaters	MAE digestion + SPME (40 min)	GC–ICP–MS	TnBP: 43% TEHP: 38%	TnBP: 8% TEHP: 4%	LOD: TnBP: 4.2 ng/L, TEHP: 3.2 ng/L	27
Surface water, wastewater	DLLME (10 min)	GC–NPD	TnBP: 94–104% TEHP: 40–114%	TnBP: 2–6% TEHP: 9–17%	LOQ: TnBP: 0.01 μg/L, TEHP: 0.08 μg/L	28

SPME: solid-phase microextraction; SPE: solid-phase extraction; MASE: membrane-assisted solvent extraction; MAE: microwave assisted extraction.ICP–MS: inductively coupled plasma mass spectrometry; DCM: dichloromethane; DLLME: dispersive liquid–liquid microextraction.ESI: electrospray ionization; NPD: nitrogen phosphorous detection; MQL: method quantification limits; N.A.: not available.

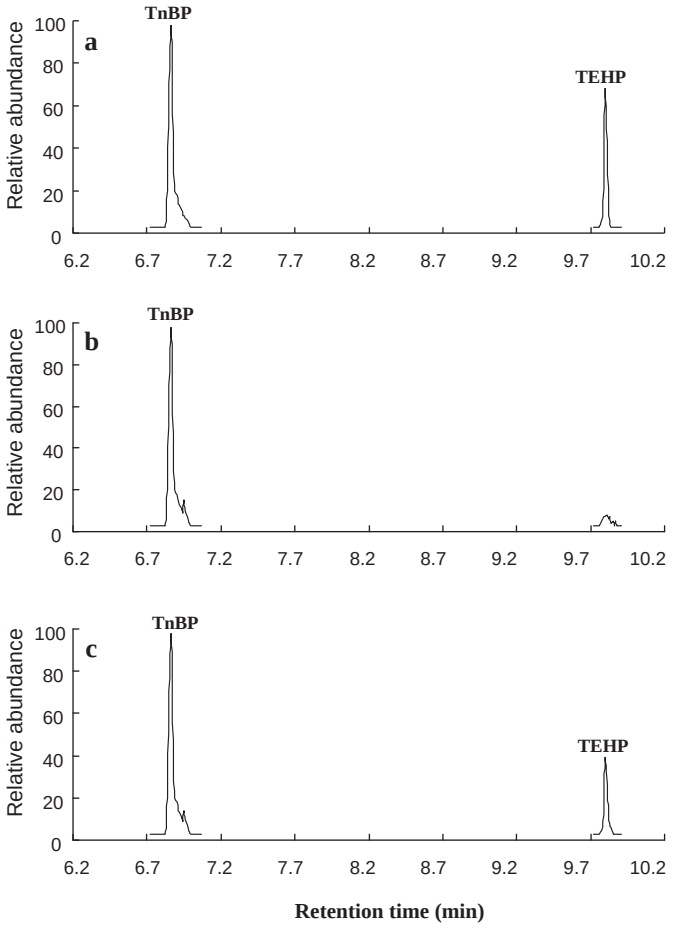

Fig. 4. GC–(EI)MS–SIM chromatograms of (a) the standards, (b) the non-spiked and (c) the spiked effluent-I samples obtained from the An-Ping WWTP.

4. Conclusions

A rapid and reliable one-step solvent-free MA-HS-SPME approach coupled with GC–MS–SIM was developed and optimized to determine the levels of selected OPEs in aqueous samples. MA-HS-SPME appears to be a good alternative extraction method for the determination of organic compounds in aqueous samples, it is a simple, effective, and eco-friendly analytical method.

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