Journal of Chromatography A, 1217 (2010) 6747–6753

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Simultaneous determination of UV filters and polycyclic musks in aqueous samples by solid-phase microextraction and gas chromatography–mass spectrometry

Hongtao Liu[a,*], Ling Liu[a], Yiquan Xiong[a], Xuemei Yang[a], Tiangang Luan[b,**]

[a] Hygiene Detection Center, School of Public Health and Tropical Medicine, Southern Medical University, Guangzhou 510515, China
[b] MOE Key Laboratory of Aquatic Product Safety, School of Marine Sciences, Sun Yat-Sen University, Guangzhou 510275, China

ARTICLE INFO

Article history:
Available online 9 June 2010

Keywords:
UV filters
Musks
Solid-phase microextraction (SPME)
Gas chromatography–mass spectrometry (GC–MS)
Matrix effect

ABSTRACT

A simple, precise and accurate method for the simultaneous determination of four UV filters and five polycyclic musks (PCMs) in aqueous samples was developed by solid-phase microextraction coupled with gas chromatography–mass spectrometry (SPME-GC–MS). The operating conditions affecting the performance of SPME-GC–MS, including fiber thickness, desorption time, pH, salinity, extraction time and temperature have been carefully studied. Under optimum conditions (30 μm PDMS fiber, 7 min desorption time, pH 7, 10% NaCl, 90 min extraction time at 24 °C), the correlation coefficients (r^2) of the calibration curves of target compounds ranged from 0.9993 to 0.9999. The limit of detection (LOD) and limit of quantification (LOQ) ranged from 0.2 to 9.6 ng L^{-1} and 0.7 to 32.0 ng L^{-1}, respectively. The developed procedure was applied to the determinations of four UV filters and five PCMs in river water samples and internal standard was used for calibration to compensate the matrix effect. Good relative recoveries were obtained for spiked river water at low, medium and high levels. The proposed SPME method was compared with traditional SPE procedure and the results found in river water using both methods were in the same order of magnitude and both are quite agreeable.

1. Introduction

Pharmaceuticals and personal care products (PPCPs) have gained increasing interest in recent years due to their huge consumption and potentially harmful concentration in aqueous environment [1,2]. UV filters and polycyclic musks (PCMs) are two important ingredients of PPCPs that have shown potential endocrine disruption properties [1–9]. Thus more attention should be paid to their impact on ecological system and human health. PCMs are widely used as fragrance ingredients in washing and cleaning agents, personal care products and in other consumables. Organic UV filters are synthetic compounds for protecting the skin from sun exposure by absorbing UV radiation. They are used in sunscreen products, cosmetics, beauty creams and skin lotions, lipsticks, hair sprays, hair dyes and shampoos. These two kinds of compounds can enter the aqueous environment directly or indirectly, for example, swimming and bathing in lakes and rivers, from showering, washing, and via wastewater treatment plants (WWTPs). Moreover, these two classes of compounds are lipophilic and therefore have potential for bioaccumulation and biomagnifications via food chain. Some of these compounds have been found in fish, urine and breast milk [10–13]. Therefore, simultaneous determination of these two classes of compounds is urgently needed when studying their environmental behavior and co-behavior, since their characters and the ways of entering into the environment are similar to each other. Recent papers have reported that some UV filters show synergistic estrogenic activity and others show antagonistic activity [9], but the co-estrogenic activity of a mixture of UV filters and polycyclic musks has not been well studied till now. Thus simultaneous determination of these classes of compounds can provide a useful tool for the research in this area.

A number of techniques, including HPLC-DAD, GC-FID, GC–MS and LC–MS [14–47], have been used for the analysis of UV filters and PCMs in different types of samples. Liquid chromatographic analysis has been used to determine several sunscreens in commercial formulations [14–18], but the detection limit was not low enough to detect low concentration levels of UV filters/PCMs at μg L^{-1} level or lower. Appropriate sample pretreatment is required to achieve reliable results, since the concentration levels of UV filters and PCMs are generally low and in complex matrices. Some methods, such as solid-phase extraction (SPE) [19–26], liquid–liquid extraction (LLE) [27], stir bar sorptive extraction (SBSE) [28,29], micelle mediated extraction [30], ultrasonic

* Corresponding author. Tel.: +86 20 61648564x6023; fax: +86 20 61648966.
** Corresponding author. Tel.: +86 20 84112958; fax: +86 20 84037549.
E-mail addresses: liu_tt@hotmail.com (H. Liu), cesltg@mail.sysu.edu.cn (T. Luan).

0021-9673/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2010.06.004

extraction (USE) [31,32], pressurized liquid extraction (PLE) or accelerated solvent extraction (ASE) [33–36], membrane-assisted liquid–liquid extraction [37,38], single-drop microextraction [39], solid-phase microextraction (SPME) [40–45] and microwave-assisted headspace solid-phase microextraction [46] have been used for sample preparation prior to the determination of UV filters or PCMs. But the applications were only limited to the determination of one class of compounds (UV filters or PCMs) or one or two target compounds. M.A. Mottaleb [47] has reported using traditional SPE and LLE for sample preparation prior to simultaneous determinations of UV filters and PCMs. However, those methods are relatively time-consuming, tedious and consuming large quantities of toxic solvents, thus environmental unfriendly. Recently a new environmental friendly technique was used for the determination of UV filters and PCMs by microextraction with packed sorbent (MEPS) [48]. The MEPS technique showed for the determination of analytes a precision of 1–12% mean relative standard deviation (RSD) whereas with SPME-GC–MS the precision was in the range of 3–5% [48]. Thus, SPME is still attractive for environmental application. SPME was introduced by Arthur and Pawliszyn in 1990 [49]. Many papers [50–55] have reported that it is an efficient extraction technique allowing simultaneous extraction and preconcentration of analytes from different sample matrices. Analytes adsorbed to the coating phase of fiber were then thermally desorbed into the injection port of gas chromatograph, and subsequently analyzed. It has the advantages of simplicity, low cost, and solvent-free. The aim of this study was to investigate the use of SPME coupling to GC/MS for simultaneous determination of four UV filters and five PCMs in aqueous samples. All the parameters influencing the performance of SPME including fiber thickness, desorption time, pH, salinity, extraction time and temperature have been carefully examined and optimized. The internal standard was used for calibration in our work to compensate the matrix effect of river water. It was successfully applied to the analysis of four UV filters and five PCMs in river water. The results agreed quite well with our previously published data obtained by SPE-GC–MS [26]. The developed method was sensitive, selective and rapid. It has broadened SPME application range for simultaneous determination of UV filters and PCMs not only in the numbers of analytes, but also in the types of aqueous samples, especially the polluted aqueous samples.

2. Experimental

2.1. Reagents

The standards of Musks, including Celestolide (ADBI), Phantolide (AHMI), Traseolide (ATII), Galaxolide (HHCB) and Tonalide (AHTN) were purchased from LGC standards GmbH (Wesel, Germany). The UV filter standards, Octyl salicylate and Octocrilene, were purchased from Sigma–Aldrich (St. Louis, MO, USA), 2-hydroxy-4-methoxybenzophenone and 3-(4-methylbenzyliden)camphor were from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Deuterated Tonalide (AHTN-d3, 10 mg L^{-1}) was purchased from Dr. Ehrendorf. The individual stock standard solution of 1 g L^{-1} for each target compound was prepared by dissolving 0.0500 g of each standard in acetone in a 50 mL volumetric flask. The 10 mg L^{-1} stock mix-standard of the above nine compounds were prepared by adding 0.1 mL of each stock standard in a 10 mL volumetric flask and diluted with acetone. The solutions were stored in the dark at 4 °C. Working standard solutions at different concentrations were freshly prepared by appropriate dilution of the stock mix-standard solution with ultra-pure water. Three milliliters of each working standard were put into 4 mL sample vials for SPME procedure. All chemicals and reagents used in this study were analytical grade. Ultra-pure water was supplied by Milli-Q apparatus.

2.2. Instrumentation and operating conditions

A Shimadzu (Japan) 2010plus gas chromatography-mass spectrometer was used for analysis. A 30 m × 0.25 mm I.D. × 0.25 μm Rtx-5MS (Restek) fused-silica capillary column, coated with 5% diphenyl and 95% dimethylpolysiloxane was employed. The column temperature program was set as follows: 120–190 °C at 10 °C min^{-1}, hold for 5 min, 190–300 °C at 10 °C min^{-1}, hold for 3 min. The total run time of the program was 26 min. The GC injector port was used in the 'splitless' mode and held isothermally at 280 °C for SPME injections for the duration of the run. Helium gas was used as the carrier gas, at a flow rate of 1 mL min^{-1} by using electronic pressure control. The GC/MS interface temperature was maintained at 280 °C. The MS was operated in the electron impact (EI) ionization mode with electron energy of 70 eV, and mass-to-charge ratio scan ranged from 50 to 550 amu to determine appropriate masses for selected ion monitoring. The MS ion source temperature was held at 200 °C.

2.3. SPME device and procedure

The SPME manual fiber holder was from Supelco Inc. (Bellefonte, PA, USA). Polydimethylsioxane fiber (PDMS, Supelco) with 30 μm thickness was used for extraction. The SPME fibers were conditioned under helium for 1 h in hot GC injection port before the first use. The SPME sampling stand and heat/stir plate used in extraction were also from Supelco. The magnetic stirring bars (10 mm × 3 mm) were from Aldrich (St. Louis, MO, USA).

The SPME device and procedure have been extensively described elsewhere [56,57]. The sampling was performed by immersing the SPME fiber directly into a 3 mL aqueous standard solution or aqueous sample for 90 min at ambient temperature (24 °C) under magnetic stirring condition for the adsorption of analytes onto the fiber coating. After extraction, the fiber was then inserted into the GC injector and the previously described GC program started immediately. Desorption time and temperature were set for 7 min at 280 °C.

2.4. Solid-phase extraction device and procedure

The solid-phase extraction (SPE) method employed was based on a previously published method [26]. The extraction of the analytes was performed with the aid of a Gilson (Middleton, WI, USA) automatic SPE apparatus (ASPEC XL), using the Cleanet 60 mg-C8 cartridges obtained from Agela Technologies (Newark, DE, USA).

The cartridge was washed with 5 mL methanol, and conditioned with 5 mL of Milli-Q water. An aliquot of 100 mL of river water was pumped through the cartridge which was then cleaned with 3 mL 40% methanol and dried under nitrogen stream. The analytes were eluted with 3 mL hexane/methylene chloride (6:4). The eluate was evaporated to dryness under a gentle stream of nitrogen at room temperature and re-dissolved with 0.5 mL hexane. Quantitation of the SPE extract was conducted using GC–MS system previously described except the GC injector port set in the 'split' mode with 10:1 splitting ratio.

3. Results and discussion

3.1. Optimization of operating conditions for SPME-GC–MS

The operating conditions affecting the performance of SPME-GC–MS, including fiber thickness, desorption time, pH, salinity,

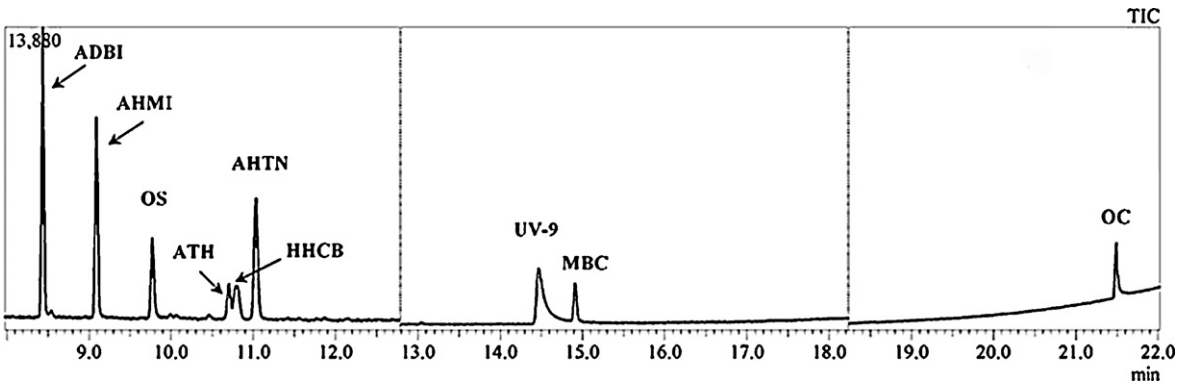

Fig. 1. TIC chromatogram of 9 target compounds under optimized GC–MS conditions.

extraction time and temperature have been carefully studied. All of the optimization experiments were conducted with 3 replicates.

3.1.1. Selection of fiber thickness and fiber carry over

Both PDMS fiber and PDMS-DVB fiber are suitable for extraction of PCMs or UV filters [40–45], if thickness would be taken into consideration. The octanol–water partition coefficients of most selected compounds are greater than 5.5. As a type of hydrophobic coating, PDMS is better than PDMS-DVB for direct extraction mode, since PDMS is a type of liquid coating, which has larger linear range than solid coatings (e.g. PDMS-DVB) and no replacement effect. Therefore, PDMS fiber was selected for the study. The thickness of PDMS fiber was further investigated.

Deuterated AHTN was used as internal standard to compensate matrix effect in analyzing real samples. Fig. 1 shows the chromatogram of target compounds (0.2 $\mu g\,L^{-1}$, pH = 7) obtained after SPME extraction procedure. All compounds were well separated under the temperature program described above. To increase sensitivity, selected ion monitoring (SIM) mode was used to quantitatively analyze UV filters and musks. The molecular weight, retention time, molecular ion and qualifier ions for each compound were listed in Table 1.

Two PDMS fibers with 100 and 30 μm thick films were employed for the study of extraction of target compounds (0.2 $\mu g\,L^{-1}$, pH = 7). The sensitivity of 30 μm PDMS fiber was proved to be high enough and the extraction and desorption time of 100 μm PDMS were quite long. Thus, 30 μm PDMS fiber was selected for the subsequent experiments.

The carry-over test was performed by placing the fiber back to the GC injector (280 °C) for another period of exposure after the previous thermo-desorption in GC injector. During the carry-over test, two compounds (octyl salicylate, octocrilene) were detected even after fourth or fifth desorption. This 'fake' carry-over was finally found to be caused by the exposure of fiber in air after thermo-desorption. Results showed that the longer the fiber was exposed to air, the larger the signal was detected. The carry-over was not caused by contaminated linear or other inlet parts of GC–MS. It was proved by the following experiment: a new fiber was conditioned at 250 °C for 1 h. Afterwards, it was immerged into a headspace sample vial filled with argon gas for 15 min, and then it was placed back into GC injector for GC–MS analysis. No signal related to target compounds was detected. Then the fiber was put in the air for 15 min and re-injected for another analysis. Signal appeared again. This suggested that there were detectable concentrations of these two compounds in the air and that SPME could be a good sampling method. Moreover, the fiber should be protected in none-air atmosphere before extracting the target compounds to avoid overestimation.

3.1.2. Effect of desorption time

The optimum desorption time was found by varying the desorption time (1, 3, 5, 7, 9, 11 min, respectively) of PDMS fiber in the GC injector at 280 °C with 0.2 $\mu g\,L^{-1}$ mix-standard solution (pH = 7). For most of the selected compounds, maximum response was found when desorption time was 7 min (Fig. 2). With such long desorption time, peak width became broader. However, the difference of peak width at baseline between 7-min desorption and 1-min desorption is about 0.1 min, which did not influence the separation. Thus, 7 min was chosen as desorption time for the subsequent experiments.

3.1.3. Effects of pH and salinity

Generally, favorable conditions for forming neutral form of target compounds should be selected in order to increase the extraction efficiencies of target compounds in sample solution. The pH value and salinity of the solution are the most important factors influencing the neutral form of target compounds, thus they should be optimized prior to further experiment. The sample solutions at pH 4, 5, 6, 7, 8 and 9 were extracted respectively for 30 min at room temperature and the desorption time was set for 7 min. The pH optimization results, depicted in Fig. 3 indicated that the solution at pH7.0 showed slightly higher response and better reproducibility. Thus, pH = 7.0 was chosen as optimum pH in this work.

Table 1
Basic information of 9 target compounds and retention time, characterized ions, quantization ion under optimized GC–MS conditions.

Compound	Abbreviation	CAS No.	Molecular weight	Retention time (min)	Quantization ion	Characterized ions
Celestolide	ADBI	13171-00-1	244	8.34	229	173,229,244
Phantolide	AHMI	15323-35-0	244	8.98	229	187,229,244
Octyl salicylate	OS	118-60-5	250	9.65	120	120,138,250
Traseolide	ATII	68140-48-7	258	10.54	215	173,215,258
Galaxolide	HHCB	1222-05-5	258	10.64	243	213,243,258
Todalide-d3	AHTN-d3	–	261	10.81	246	190,246,261
Tonalide	AHTN	1506-02-1	258	10.85	243	187,243,258
2-Hydroxy-4-methoxybenzophenone	UV-9	131-57-7	227	14.31	227	151,227,228
3-(4-Methylbenzyliden)camphor	MBC	36861-47-9	254	14.77	254	211,239,254
Octocrilene	OC	6197-30-4	361	21.36	204	204,249,306

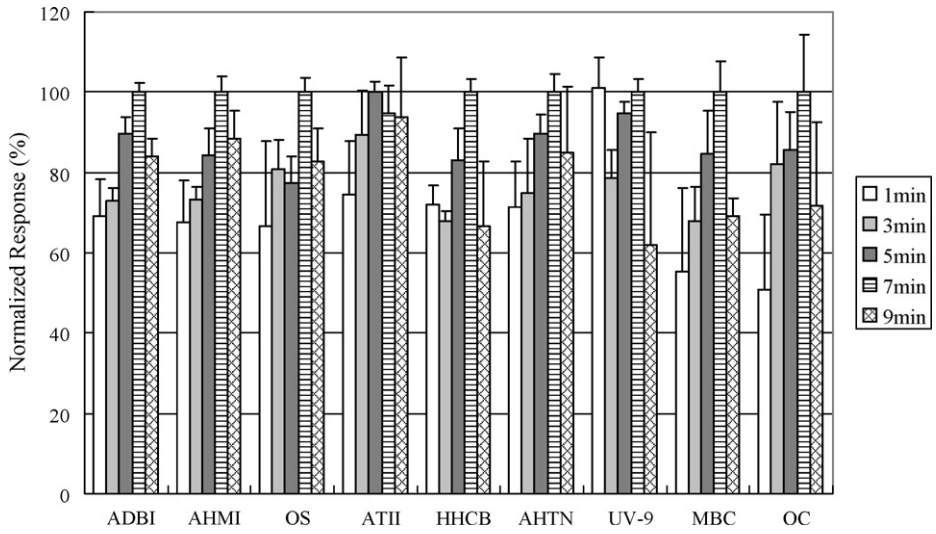

Fig. 2. Effect of desorption time on the detector response (normalized to the individual maximum response), 0.2 μg L^{-1} mix-standard, extraction time 30 min, pH = 7, 0% NaCl, room temperature, n = 3.

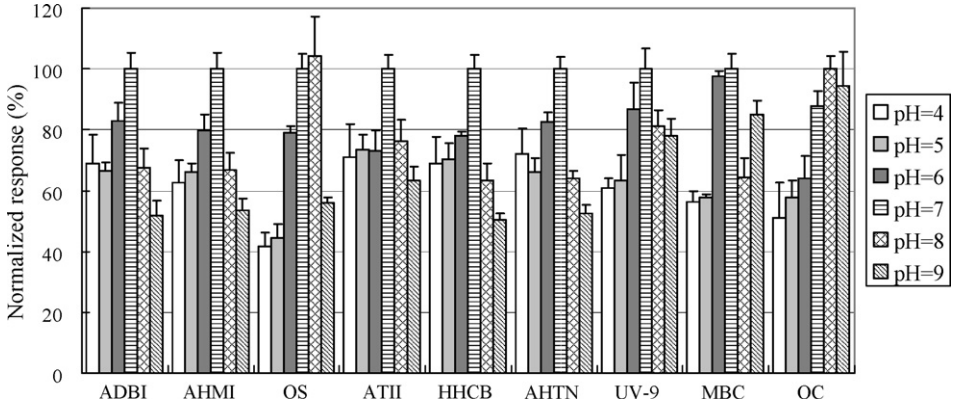

Fig. 3. Effect of pH on the normalized detector response, 0.2 μg L^{-1} mix-standard, extraction time 30 min, 0% NaCl, room temperature, n = 3.

The extraction efficiency of the fiber will be affected by the salt content in the sample solution by the variation of the solubility of compounds in aqueous phase. The effect of the salinity of the sample solution was studied by spiking 0%, 5%, 10%, 15%, 20% and 25% of NaCl into the sample solutions. During the procedure, the adsorption was kept at room temperature for 30 min, and the solution at pH 7. The results were depicted in Fig. 4. It was observed that, for most of the selected compounds, the responses reached maximum at 10% NaCl, except for UV-9 and OC. The possible reason for this phenomenon that extraction efficiency increased firstly with increase of salt content and then deceased with further increase of salt content could be explained by "salt-out" effect and reverse "salt in" effect. Normally, salt content influences the extraction efficiency by so-called 'salt-out effect', i.e. salt would decrease the solubility

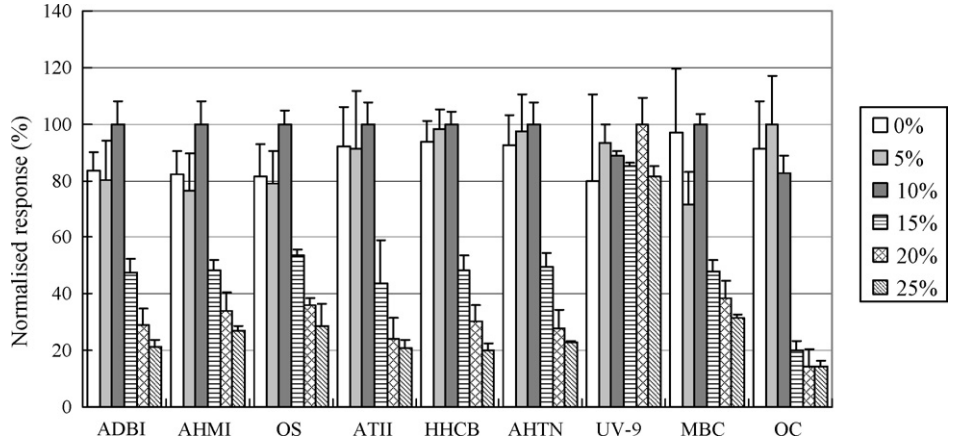

Fig. 4. Effect of salinity on the normalized detector response, 0.2 μg L^{-1} mix-standard, extraction time 30 min, pH = 7, room temperature, n = 3.

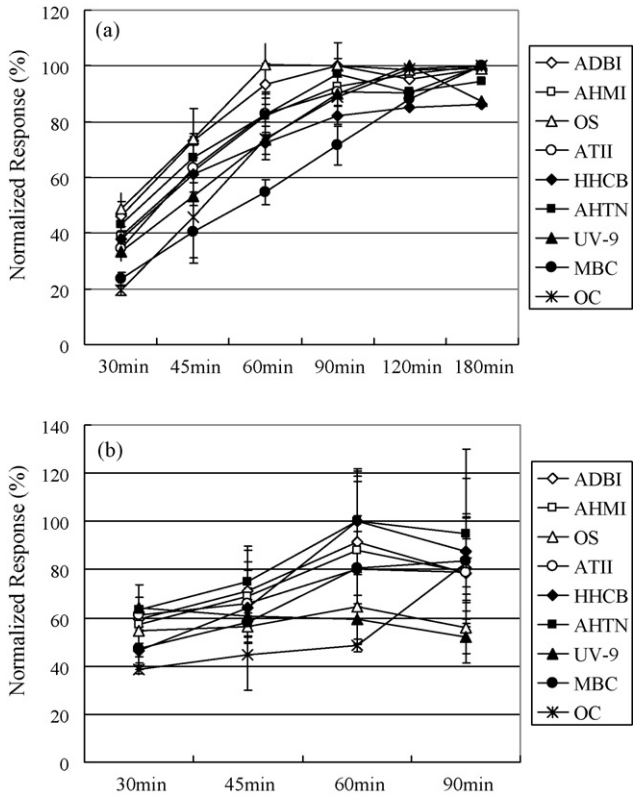

Fig. 5. Detector response vs. extraction time under different temperatures: (a) room temperature (24 °C), (b) 45 °C; both (a) and (b) were normalized to the same scale; 0.2 μg L^{-1} mix-standard, pH = 7, 10% NaCl, n = 3 (except response with 120 min, 180 min extraction time under room temperature).

of target compound in aqueous phase, thus increase the partition coefficient between fiber coating and aqueous phase. However, in some cases, the solubility of the compounds might not change, the addition of salt may decrease the amount of extracted by decreasing the activity coefficients of the analytes [57]. Considering the overall responses of the target compounds, a concentration level of 10% NaCl was selected.

3.1.4. Effect of extraction time and temperature

The standard solution of 0.2 μg L^{-1} target compounds (pH = 7, 10% NaCl) was used to investigate the optimum conditions for SPME procedure under different temperatures. The equilibrium time for SPME depends on the rate of mass transfer in the aqueous phase. The optimum extraction time and temperature were determined by varying the extraction time from 30 to 180 min at 24 and from 30 to 90 min at 45 °C, respectively. A constant rapid stirring was employed to increase the rate of mass transfer in aqueous phase. As shown in Fig. 5 (both a and b were normalized to the same scale, i.e. the results were normalized to the maximum response of each target compound either at 24 or at 45 °C), at 24 °C, the amount of most target compounds extracted increased with the increase of extraction time, but was in equilibrium at about 120 min. At 45 °C, the responses of selected compounds tended to increase slightly but showed bad reproducibility. The response of most of the selected compounds at 45 °C was smaller than those at 24 °C, this might be due to the decrease of solid–liquid partition coefficient at higher temperature. At 24 °C, the response at 90 min extraction did not differ too much as 120 min. Therefore, 90 min extraction time is long enough to get good sensitivities. Considering the overall responses of the target compounds, the optimum extraction time and temperature were set at 90 min and 24 °C, respectively.

3.2. Linear range and detection limit

The SPME procedure was performed according to the optimized conditions. The electron impact ionization and selected ion monitoring mode were used to determine the detection limit of selected compounds in aqueous solution. Internal standard calibration was employed to adapt the method to the different samples with different matrices. AHTN-d3 (1 μg L^{-1}) was selected as internal standard. The concentrations of working solutions were selected to be 0.01, 0.05, 0.1, 0.5, 1, 5 and 10 μg L^{-1}, respectively. The limits of detection (LOD) and limits of quantification (LOQ) of selected compounds were calculated based on the 3σ criteria and 10σ criteria, respectively. The results are showed in Table 2. The linear ranges of target compounds by SPME procedure spanned over 3 orders of magnitude, with correlation coefficients ranging from 0.9993 to 0.9999. The results were compared with those obtained by SPE-GC–MS method published previously (Table 2). The sensitivities were still better than SPE-GC–MS even with 200-time concentration by SPE. Concentration factor of SPE could be increased further by using large sample volume. However, the cartridge would be easily blocked, especially for polluted aqueous sample. Moreover, it would be an extreme labor- and time-consuming work if we use large sample volume in SPE.

3.3. Determination of UV filters and PCMs in river water

3.3.1. Matrix effect and its compensation

River water was selected as real sample for evaluation of the developed method. For aqueous environmental sample, the matrix effect was not observed in the former publication. It's probably due to that the samples they used were not polluted seriously. However, the environmental aqueous samples would differ in locations,

Table 2
The linearity of calibration curve, the limit of detection (LOD) and the limit of quantification (LOQ) of 9 target compounds under optimized SPME-GC–MS and comparison of results with those by SPE-GC–MS.

Compound	Results by SPE-GC–MS				Results by SPME-GC–MS			
	Linear range (μg L^{-1})	Correlation coefficient r^2	LOD[a] (ng L^{-1})	LOQ[a] (ng L^{-1})	Linear range (ng L^{-1})	Correlation coefficient r^2	LOD (ng L^{-1})	LOQ (ng L^{-1})
ADBI	10–1000	0.9999	5.15	17.2	0.01–10	0.9994	1.2	4.2
AHMI	10–1000	0.9996	5.29	17.6	0.01–10	0.9994	1.0	3.3
OS	10–1000	0.9998	24.8	82.6	0.01–10	0.9993	0.5	1.7
ATII	20–1000	0.9996	25.7	85.7	0.01–10	0.9995	9.6	32.0
HHCB	10–1000	0.9998	25.4	84.8	0.01–10	0.9997	0.4	1.3
AHTN	10–1000	0.9996	10.8	35.9	0.01–10	0.9994	0.5	1.7
UV-9	50–1000	0.9995	85.2	284	0.01–10	0.9999	0.2	0.7
MBC	20–1000	0.9996	21.0	70.2	0.01–10	0.9996	1.3	4.2
OC	50–1000	0.9993	42.9	143	0.01–10	0.9993	2.0	6.7

[a] Results after multiplying concentration factor (200-time concentrated by SPE).

Table 3
Concentration of target compounds, relative recoveries of target compounds by optimized SPME-GC–MS method and comparison of results with those by SPE-GC–MS.

Compound	Results by SPE-GC–MS	Results by SPME-GC–MS					
	River water ($\mu g\,L^{-1}$, $n=3$)	River water ($\mu g\,L^{-1}$, $n=3$)	Add 0.05 ($\mu g\,L^{-1}$, $n=3$) mix-standard ($\mu g\,L^{-1}$, $n=3$)	Relative recoveries (%)	Add 0.5 $\mu g\,L^{-1}$ mix-standard ($\mu g\,L^{-1}$, $n=3$)	Relative recoveries (%)	Add 5 $\mu g\,L^{-1}$ mix-standard ($\mu g\,L^{-1}$, $n=3$)	Relative recoveries (%)
ADBI	0.011 ± 0.002	0.012 ± 0.001	0.044 ± 0.003	64.4	0.46 ± 0.02	90.3	5.90 ± 0.19	117
AHMI	0.013 ± 0.001	0.011 ± 0.001	0.045 ± 0.001	68.7	0.46 ± 0.01	89.1	5.90 ± 0.13	117
OS	n.d.	0.008 ± 0.001	0.046 ± 0.002	75.4	0.43 ± 0.06	84.3	5.62 ± 0.54	112
ATII	n.d.[a]	n.d.	0.045 ± 0.002	89.5	0.53 ± 0.02	105	5.85 ± 0.18	117
HHCB	0.60 ± 0.06	0.52 ± 0.05	0.57 ± 0.01	103	0.93 ± 0.01	82.0	6.33 ± 0.24	116
AHTN	0.036 ± 0.003	0.032 ± 0.003	0.067 ± 0.009	72.0	0.51 ± 0.00	95.4	5.92 ± 0.08	117
UV-9	n.d.	0.059 ± 0.005	0.099 ± 0.006	80.3	0.43 ± 0.01	73.6	5.39 ± 0.28	106
MBC	n.d.	0.010 ± 0.001	0.046 ± 0.002	72.5	0.41 ± 0.02	79.7	5.79 ± 0.04	115
OC	n.d.	0.029 ± 0.003	0.085 ± 0.011	114	0.53 ± 0.07	100	5.18 ± 0.42	103

[a] Not detected.

in season, in type, etc. Thus, matrix effect might be encountered during SPME-GC–MS determination. The river water was sampled near the first affiliated hospital of Southern Medical University. It was light yellow, stinking and the DOC value was greater than 20 mg L^{-1}, indicating the river was polluted seriously. To investigate the matrix effect, response of river water, spiked river water without internal standard as well as aqueous standard was used to calculate matrix factor. The matrix factor was defined as Eq. (1). The more its value far away from 1, the more prominent the matrix effect is

$$\text{matrix factor} = \frac{A_{sample+s} - A_{sample}}{A_s} \quad (1)$$

where $A_{sample+S}$ is the integration area of quantization ion of spiked river water. A_{sample} is the integration area of quantization ion of river water, and A_s is the integration area of quantization ion of standard solution whose concentration is equal to spiked concentration.

The matrix factors of target compounds in river water we sampled were in the range of 0.4–0.5, which means matrix effect do exist in the river water we selected. Thus, use of internal standard becomes significant and necessary.

3.3.2. Determination of UV filters and PCMs in river water

Under optimized conditions, the concentrations of selected nine compounds in river water were determined by SPME-GC–MS with internal standard calibration. Results are shown in Table 3. Except for ATII, eight of selected compounds were detected by the developed SPME-GC–MS method. To further evaluate the validation of selection of internal standard as well as the developed method, the relative recovery test was performed by spiking mix-standards of selected compounds into river water at low (0.05 $\mu g\,L^{-1}$), medium (0.5 $\mu g\,L^{-1}$) and high levels (5 $\mu g\,L^{-1}$). The relative recovery was defined as Eq. (1)

$$\text{relative recovery}\,(\%) = \frac{C_{sample+s} - C_{sample}}{C_s} \times 100\% \quad (2)$$

where $C_{sample+S}$ is the measured concentration of spiked river water by internal standard calibration method. C_{sample} is the measured concentration of river water by internal standard calibration method and C_s is spiked concentration.

Relative recoveries of selected compounds ranged from 64.4% to 117% (Table 3). The precision was also evaluated by performing three replicates from river water as well as samples for recovery test. The relative standard deviation (RSD, $n=3$) of most target compounds was less than 10%, showing good reproducibility for all target compounds. The results obtained for the target compounds in river water by the developed SPME-GC–MS method were also compared with those obtained by SPE-GC–MS method published previously [26]. Both results agreed quite well except for OS, UV-9, MBC and OC compounds, since their concentrations were too low to be detected by described SPE-GC–MS method in Section 2.4.

4. Conclusions

A simple, sensitive and selective method for the determination of five PCMs and four UV filters in aqueous sample has been developed by SPME coupled with GC–MS. A 30 μm polydimethylsioxane coated fiber could be used to give a limit of detection (LOD) and limit of quantification (LOQ) of target compounds ranging from 0.2 to 9.6 ng L^{-1} and 0.7 to 32.0 ng L^{-1}, respectively. This method has exhibited adequate precision and linearity and was successfully applied to the analysis of UV filters and PCMs in river water with satisfied relative recoveries for low, medium, high levels of concentration. The results agreed quite well with those obtained by SPE-GC–MS.

Acknowledgements

Financial support from the National Natural Science Foundation of China (NSFC, No. 40601090 and No. 20977116) and the Guangdong Provincial Natural Science Foundation of China (No. 9151027501000114) as well as proofreading by Professor Zhanxia Zhang and Gangfeng Ouyang are gratefully acknowledged.

References

[1] C.G. Daughton, T.A. Ternes, Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? (EPA special report), http://epa.gov/nerlesd1/chemistry/pharma/new.htm.
[2] T. Soeborg, L.H. Basse, B. Halling-Sorensen, Toxicology 236 (2007) 140.
[3] F. Balk, R.A. Ford, Toxicol. Lett. 111 (1999) 57.
[4] D.L. Giokas, A. Salvador, A. Chisvert, Trends Anal. Chem. 26 (2007) 360.
[5] G.J. Nohynek, H. Schaefer, Regul. Toxicol. Pharmacol. 33 (2001) 285.
[6] J.W. Tas, F. Balk, R.A. Ford, E.J. vandPlassche, Chemosphere 35 (1997) 2973.
[7] D.T. Salvito, R.J. Senna, T.W. Federle, Environ. Toxicol. Chem. 21 (2002) 1301.
[8] D.T. Salvito, M.G.H. Vey, R.J. Senna, Flavour Frag. J. 19 (2004) 105.
[9] R.H.M.M. Schreurs, E. Sonneveld, J.H.J. Jansen, W. Seinen, B. van der Burg, Toxicol. Sci. 83 (2005) 264.
[10] M.E. Balmer, H.R. Buser, M.D. Muller, T. Poiger, Environ. Sci. Technol. 39 (2005) 953.
[11] K. Fent, P. Kunz, M. Wolf, H. Schmutz, D. Gygax, C. Schanne, Chimia 58 (2004) 325.
[12] T. Kupper, C. Plagellat, R.C. Braendli, L.F. de Alencastro, D. Grandjean, J. Tarradellas, Water Res. 40 (2006) 2603.
[13] T. Poiger, H.R. Buser, M.E. Balmer, P.A. Bergqvist, M.D. Muller, Chemosphere 55 (2004) 951.
[14] A. Chisvert, A. Salvador, J. Chromatogr. A 977 (2002) 277.
[15] D.J. Schakel, D. Kalsbeek, K. Boer, J. Chromatogr. A 1049 (2004) 127.
[16] A. Chisvert, M.C. Pascual-Martí, A. Salvador, J. Chromatogr. A 921 (2001) 207.
[17] C.G. Smyrniotakis, A. Helen, Archontaki, J. Chromatogr. A 1031 (2004) 319.
[18] A.B. Martínez-Girón, A.L. Crego, M.J. González, M.L. Marina, J. Chromatogr. A 1217 (2010) 1157.
[19] A. Zenker, H. Schmutz, K. Fent, J. Chromatogr. A 1202 (2008) 64.
[20] D.L. Giokas, V.A. Sakkas, T.A. Albanis, J. Chromatogr. A 1026 (2004) 289.
[21] L.I. Osemwengie, S. Steinberg, J. Chromatogr. A 932 (2001) 107.
[22] K. Bester, J. Chromatogr. A 1216 (2009) 470.
[23] M.C. Pietrogrande, G. Basaglia, F. Dondi, J. Sep. Sci. 32 (2009) 1249.
[24] Y. Lv, T. Yuan, J.Y. Hu, W.H. Wang, Anal. Sci. 25 (2009) 1125.
[25] R. Rodil, S. Schrader, M. Moeder, Rapid Commun. Mass Spectrom. 23 (2009) 580.
[26] F.J. Sheng, H.F. Wang, C. Lv, Y.L. Zhang, H.T. Liu, Fenxi Ceshi xuebao 28 (2009) 900 (Chinese).
[27] H.K. Jeon, Y. Chung, J.C. Ryu, J. Chromatogr. A 1131 (2006) 192.
[28] R. Rodil, M. Moeder, J. Chromatogr. A 1179 (2008) 81.
[29] M. Kawaguchi, R. Ito, H. Honda, N. Endo, N. Okanouchi, K. Saito, Y. Seto, H. Nakazawa, J. Chromatogr. A 1200 (2008) 260.
[30] D.L. Giokas, V.A. Sakkas, T.A. Albanis, D.A. Lampropoulou, J. Chromatogr. A 1077 (2005) 19.
[31] T.A. Ternes, M. Bonerz, N. Herrmann, D. Löffler, E. Keller, B.B. Lacida, A.C. Alder, J. Chromatogr. A 1067 (2005) 213.
[32] J. Pablo Lamas, L. Sanchez-Prado, C. Garcia-Jares, M. Llompart, J. Chromatogr. A 1217 (2010) 1882.
[33] L.I. Osemwengie, S. Steinberg, J. Chromatogr. A 993 (2003) 1.
[34] A. Nieto, F. Borrull, R.M. Marce, E. Pocurull, J. Chromatogr. A 1216 (2009) 5619.
[35] R. Rodil, S. Schrader, M. Moeder, J. Chromatogr. A 1216 (2009) 8851.
[36] R. Draisci, C. Marchiafava, E. Ferretti, L. Palleschi, G. Catellani, A. Anastasio, J. Chromatogr. A 814 (1998) 187.
[37] T. Einsle, H. Paschke, K. Bruns, S. Schrader, P. Popp, M. Moeder, J. Chromatogr. A 1124 (2006) 196.
[38] R. Rodil, S. Schrader, M. Moeder, J. Chromatogr. A 1216 (2009) 4887.
[39] L. Vidal, A. Chisvert, A. Canals, A. Salvador, J. Chromatogr. A 1174 (2007) 95.
[40] D.A. Lambropoulou, D.L. Giokas, V.A. Sakkas, T.A. Albanis, M.I. Karayannis, J. Chromatogr. A 967 (2002) 243.
[41] M. Llompart, C. García-Jares, C. Salgado, M. Polo, R. Cela, J. Chromatogr. A 999 (2003) 185.
[42] C. García-Jares, M. Llompart, M. Polo, C. Salgado, S. Macías, R. Cela, J. Chromatogr. A 963 (2002) 277.
[43] M. Winkler, J.V. Headley, K.M. Peru, J. Chromatogr. A 903 (2000) 203.
[44] J. Regueiro, C. Garcia-Jares, M. Llompart, J.P. Lamas, R. Cela, J. Chromatogr. A 1216 (2009) 2805.
[45] N. Negreira, I. Rodriguez, M. Ramil, E. Rubi, R. Cela, Anal. Chim. Acta 638 (2009) 36.
[46] Y.C. Wang, W.H. Ding, J. Chromatogr. A 1216 (2009) 6858.
[47] M.A. Mottaleb, S. Usenko, J.G. O'Donnell, A.J. Ramirez, B.W. Brooks, C.K. Chambliss, J. Chromatogr. A 1216 (2009) 815.
[48] M. Moeder, S. Schrader, U. Winkler, R. Rodil, J. Chromatogr. A 1217 (2010) 2925.
[49] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[50] C. Grote, K. Levsen, in: J. Pawliszyn (Ed.), Application of SPME, Royal Society of Chemistry, Cambridge, 1999, p. 169.
[51] H. Kataoka, H.L. Lord, J. Pawliszyn, J. Chromatogr. A 880 (2000) 35.
[52] F.M. Musteata, J. Pawliszyn, Trends Anal. Chem. 26 (2007) 36.
[53] S. Risticevic, V.H. Niri, D. Vuckovic, J. Pawliszyn, Anal. Bioanal. Chem. 393 (2009) 781.
[54] L.H. Yang, C.Y. Lan, H.T. Liu, J. Dong, T.G. Luan, Anal. Bioanal. Chem. 386 (2006) 391.
[55] L.H. Yang, T.G. Luan, C.Y. Lan, J. Chromatogr. A 1104 (2006) 23.
[56] J. Pawliszyn, Solid Phase Microextraction: Theory and Practice, Wiley-VCH Inc., New York, 1997.
[57] J. Pawliszyn (Ed.), Handbook of Solid Phase Microextraction, Chemical Industrial Press, Beijing, 2009.