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Gas chromatographic determination of 2-hydroxy-4-methoxybenzophenone and octyldimethyl-*p*-aminobenzoic acid sunscreen agents in swimming pool and bathing waters by solid-phase microextraction

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Abstract

A method has been developed for the trace determination of two sunscreen constituents (2-hydroxy-4-methoxybenzophenone and octyldimethyl-*p*-aminobenzoic acid) in water samples, which are commonly used in commercial formulations. The method employs solid-phase microextraction (SPME) and gas chromatography with flame ionization and mass spectrometric detection. The technique was developed with headspace and direct sampling in order to demonstrate the applicability of these SPME extraction modes for the identification of these two UV absorbing compounds in waters. The main parameters affecting the SPME process, such as desorption time, extraction time profile, salt additives, pH, and temperature, were investigated. The poly(dimethylsiloxane) 100-μm and polyacrylate 85-μm fiber coatings were found to be the most efficient for the extraction of these compounds from aqueous matrices. Linear calibration curves in the wide range of 10–500 μg/l were obtained for both compounds yielding typical RSD values of 5–9% for both extraction modes. The recoveries were relatively high, 82–98%, with quantitation limits below 1 μg/l. A comparison between the proposed methods and the conventional multiresidue solid-phase extraction revealed that the proposed technique(s) can be reliably used for sunscreen residue measurement in water samples with satisfactory results.

Keywords: Water analysis; Headspace analysis; Solid-phase microextraction; Hydroxymethoxybenzophenone; Octyldimethylaminobenzoic acid; Sunscreen agents

1. Introduction

Besides the well-recognized conventional ‘‘priority’’ pollutants (pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, etc.) the existence and transportation pathways of pharmaceuticals and active ingredients in personal care products (drugs, fragrances etc.) into the aquatic environment has been continuously receiving particular attention [1,2]. Since the first report concerning the occurrence of pharmaceutical residues in the environment [3], many studies worldwide confirmed the presence of several pharmaceutical and related compounds in treated and untreated sewage effluent [4], surface water [5,6], groundwater and drinking water [2,7].

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The major issue regarding these compounds (usually termed as PPCPs, pharmaceutical and personal care products) as an emerging environmental issue is that they are intended to exert a biological effect [8]. At present, the number of papers on this topic is quite limited and there are no extensive monitoring surveys on the occurrence and exposure routes of PPCPs, their ecological persistence or the kinds and amounts of these substances that have negative effects on people and other living organisms [7].

Besides drugs and related pharmaceutical compounds, several other substances may be released into the environment through human activities including UV absorbing chemicals from sunscreens. Studies have shown that water immersion of the skin, to which a commercial sunscreen formulation had been applied, results in sunscreen loss from the skin surface [9]. Products claiming to be waterproof or water-resistant generally have 50–80% water resistance retention (WRR) after four immersions in water, while these that do not claim similar properties, such as day-care products, sunscreen sprays and various commercialized sunscreen formulations, are readily washed-off, having a WRR of 10–30% after one single immersion [9]. In most of the cases, washing off of these products occurs for the formulation as a whole and not just for specific active ingredients [9]. As these estimations have been derived from controlled laboratory experiments rather than field data [9,10] their results are prone to uncertainties induced by the fact that water immersion on the skin in real life situations depends on the activity of each individual person during bathing activity. This is supported by relative studies, which showed that water and bathing activities may advocate to further washing-off of these products [10].

Although several studies have been focused on the emerging issue of pharmaceuticals into the aquatic environment [11], to the best of our knowledge, no previous study has ever been targeted in the investigation of sunscreen residuals in natural waters. One possible explanation is that no analytical methodology is still available allowing for the quantification of these substances at the μg/l levels. At present, most of the studies have been focused on the liquid chromatographic analysis of several sunscreen agents in commercial formulations as well as in human plasma and urine [12–15], while more selective methodologies have also been presented [16,17]. However, the majority of these methods have high detection limits (in the mg/l levels) thus limiting their applicability to sunscreen formulations or spiked biological fluids (for the investigation of matrix effects) where the content of these compounds is usually high. Only a few studies employing conventional solid-phase extraction (SPE) enrichment prior to LC or GC–MS techniques have been shown to conveniently determine such compounds in the μg/l levels but these studies were not aiming at such application. Rather some cosmetic related products were co-determined in the samples [4].

Besides the conventional SPE, solid-phase microextraction (SPE) is a technique with continuously expanding field of application due to its distinct advantages, like simplicity and rapidity of the analysis, solvent-free extraction and small sample volume. Over the past decade, the SPME related methods (direct or headspace) have been applied for the trace determination of various organic micropollutants [18–20] and more recently, for the determination of organophosphorus pesticides [21] and fungicides [22]. Both techniques rely on an equilibrium process that involves partitioning (diffusion) of the analytes from a liquid sample into the polymeric phase according to their partition coefficients thus eliminating the separate concentration step from the SPE and liquid–liquid extraction (LLE) methods. Detailed theory of the SPME absorption process and experimentation has been reported previously in precious detail [23]. Direct SPME has also been described for the determination of benzophenone in aquatic-based matrices (urine) at the μg/l levels but no special reference for water quality monitoring application has been made [24]. Rather, water was a medium for the optimization of the analytical conditions prior to a successful application in human urine.

Considering the lack of published work on the determination of UV-filters in natural waters and at the μg/l levels, the present work: (1) develops the experimental conditions for two gas chromatographic methods for the determination of two widely used sunscreen compounds, 2-hydroxy-4-methoxybenzophenone (Bz-3) and octyldimethyl-*p*-aminobenzoic acid (PABA) at the μg/l levels by exploiting the

analytical merits of the direct (DI) SPME, and headspace (HS) SPME methodologies; (2) applies both methods for the measurement of these sunscreen agents in swimming pool waters and seawater, and evaluates their efficiency compared to a reference SPE technique, and (3) tests them for accuracy by fortifying several different matrices with Bz-3 and PABA. The selection of the compounds presented in this study, over the range of commercially applicable UV filters, was based on the fact that they have been linked to several toxicological effects. More specifically, in 13-week studies of the US National Toxicology Program, the oral administration of 2-hydroxy-4-methoxybenzophenone has been linked to hepatocellular hypertrophy in mice and rats as well as to cholestatic liver injury and renal damage in rats [25]. Furthermore, PABA compounds have been linked to several toxicological effects while found to produce cytotoxic singlet molecular oxygen in sunlight illuminated aqueous solutions [26]. From an analytical standpoint, this is the first time that two different methods have been developed for sunscreen analytes measurements and confirmation in natural waters.

2. Experimental

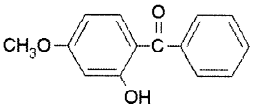
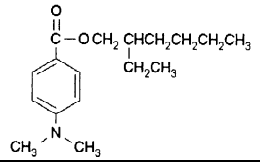
2.1. Reagents

The tested sunscreen agents—2-hydroxy-4-methoxybenzophenone, benzophenone (Bz) and octyldimethyl-*p*-aminobenzoic acid (PABA)—as shown by the structural formula in Table 1, were purchased from Aldrich (Athens, Greece). Stock standard solutions were prepared in methanol. Working standard solutions in the range of 10–500 μg/l were prepared with appropriate dilution in doubly distilled water. All standard and working solutions were stored in dark at 4 °C. The solvents used (methylene chloride, methanol, acetone) were of the highest available purity (HPLC grade) and were obtained by from Pestiscan (Labscan, Dublin, Ireland). Sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) was supplied from Merck (Darmstadt, Germany).

2.2. Equipment

The SPME device for manual extraction, consisted of a holder assembly and several replaceable fiber assemblies, was purchased from Supelco (Bellefonte, PA, USA). The fiber coatings assayed were: polyacrylate (PA 85 μm), polydimethylsiloxane (PDMS 100 μm), Carbowax–divinylbenzene (CW–DVB 65 μm) and polydimethylsiloxane–divinylbenzene (PDMS–DVB 65 μm). The fibers were conditioned prior to use as recommended by the manufacturer by heating them at different temperatures (250–300 °C) for periods between 30 min and 2 h in the GC injection port. Clear glass vials (8 ml) were used to perform SPME while magnetically stirred.

Table 1
Physicochemical properties of 2-hydroxy-4-methoxybenzophenone and PABA: chemical structure, molecular mass, octanol–water partition coefficients (K_{ow})

Compounds	Chemical structure	Molecular mass	Log K_{ow} [a]
Benzophenone-3		228.25	3.52
Octyldimethyl-PABA		277.41	5.76

[a] From Ref. [28].

2.3. Gas chromatography

Chromatographic analyses were performed using a Shimadzu 14A series gas chromatograph, equipped with a splitless injector and a flame ionization detection (FID) system. Analytes were separated with a DB-5 [poly(dimethyldiphenylsiloxane) containing 5% diphenylsiloxane] column (J&W Scientific, Folsom, CA, USA), 30 m×0.32 mm I.D., with a film thickness of 1 μm. The temperature program used for the analysis was as follows: initial temperature at 150 °C, held for 2 min, ramped at 5 °C/min to 200 °C, held for 8 min, to 210 °C at 1 °C/min, held for 2 min and 10 °C/min to 270 °C, held for 4 min. Helium was used as the carrier (1.5 ml/min) and the make up gases (40 ml/min), respectively. The detector gases were hydrogen and air and their flow-rates were regulated at 500 and 45 ml/min, respectively. The detector temperature was set to 250 °C and the injector temperature to 240 °C.

GC–MS experiments were performed on a QP 5000 Shimadzu instrument equipped with a DB-5-MS capillary column (J&W Scientific), 30×0.25 mm, 0.25 μm, containing 5% (phenyl)-methylpolysiloxane at the following chromatographic conditions: injector temperature 220 °C, oven temperature program 150 °C, held for 2 min, ramped at 20 °C/min to 150 °C, held for 2 min, to 250 °C at 20 °C/min, held for 12 min and 20 °C/min to 270 °C, held for 3 min. Helium was used as the carrier gas at a flow of 1 ml/min. The interface was kept at 290 °C and mass spectra were obtained at 70 eV.

To achieve better detection limits and enhanced selectivity, analyses were performed in the selected ion monitoring (SIM) mode. Three ions were selected from the spectrum of each compound in order to quantify the response under SIM mode: 151(100), 227(91) and 228(56) for Bz-3, 165(100), 148(39) and 277(11) for PABA. The values in parentheses give the relative abundance (%) of each peak in the spectrum.

2.4. SPE method

The SPE method employed was based on a previously described protocol for benzophenone-4 [24]. The extraction of the analytes was performed with the aid of a J.T. Baker (Thessaloniki, Greece) SPE apparatus, using the 500-mg C_{18} cartridges obtained from Chromabond (Macherey–Nagel, Düren, Germany).

The procedure consisted of washing the disk with 10 ml methylene chloride, then conditioning with 10 ml of methanol followed by 10 ml of deionized water. Next, an aliquot of 10 ml of spiked swimming pool water or sea-water was pumped through the disk. The disk was dried under vacuum from 10 min. The analytes were extracted with two consecutive 5-ml aliquots of methylene chloride. The combined extracts were evaporated to dryness under a gentle stream of nitrogen at room temperature and redissolved to 0.1 ml with methanol. Quantitation of the SPE extract was conducted using the GC–FID and GC–MS system previously described.

2.5. DI-SPME

Five ml volume of water samples was placed in 8-ml vials, sealed with PTFE-lined septa. The samples were stirred before and during extraction. The fiber was exposed to the aqueous phase for an appropriate time period of 45 min, with stirring rate of 960 rpm at room temperature (25±2 °C). After extraction, the fiber was directly exposed to the hot injector of the GC systems for analysis. Thermal desorption was carried out for 8 min. After this period no significant blank values were observed. The overall methanol concentration during these experiments was less than 0.1% (v/v) in all cases. A typical GC–FID chromatogram obtained from spiked uncontaminated swimming pool water by PDMS 100-μm fiber is shown in Fig. 1.

2.6. HS-SPME

Five ml of water samples were placed in 8-ml crimp-top headspace vials, sealed with open centered aluminum caps and PTFE-gray butyl septa spiked with appropriate amount of the standard solutions of sunscreens and mixed with 25% g/l NaCl. Sample vials were heated by supporting them with a clamp in a water bath on top of the hot-plate stirrer. Sample vials in the water bath were placed on a large silicone septum to insulate the vials from the surface of the hot-plate. After 10 min, the needle of the

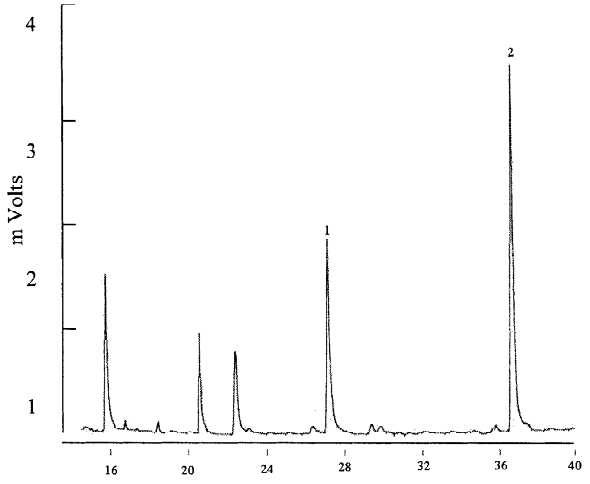


Fig. 1. A typical GC–FID chromatogram of benzophenone-3 and octyldimethyl-PABA obtained by spiking uncontaminated swimming pool water with 100 μg/l of each compound. Fiber PDMS 100 μm, extraction time 45 min, direct SPME mode: 1=Bz-3, 2=PABA.

SPME device pierced the septum of the vial and the fiber was exposed for 45 min to the headspace of the vial, above the spiked water which was kept at (90±1 °C) and stirred by a small PTFE-coated bar. Finally the fiber was retracted into the needle, pulled out from the vial and immediately inserted into the hot injector of the GC systems for analysis. Thermal desorption of sunscreens was carried out for 8 min.

3. Results and discussion

The optimum experimental conditions for the extraction and quantitation of both selected analytes were investigated by means of a univariate experimental design procedure and the results are presented below. For the method development procedure, four commercial SPME fibers (100-μm PDMS, a 85-μm PA, a 65-μm PDMS–DVB and 65-μm CW–DVB) covering a wide range of polarities, were compared for their extraction efficiency and carryover of Bz-3 and PABA. Based on the criteria of the analyte extraction efficiency, the reproducibility of SPME technique with the above coatings [21,22] and their fouling resistance after repeated uses [23], the PDMS and PA fibers were selected for the subsequent experimental design procedure.

3.1. Carryover effect

The amount of analytes desorbed increased with an increasing desorption time and the lower carryover was generally observed with the PA 85-μm fiber. After a 4-min desorption, the amount remaining on the fibers drops to 1–4%. By increasing the desorption time to 8 min, the carryover levels off to <1% for both fibers and it was therefore selected.

3.2. Extraction temperature

Since extraction is an exothermic process, its effect was considered trivial for the DI mode extraction procedure, aiming at the same time at the investigation of the possibility for in-field application. For the headspace extraction though, temperature controls the diffusion of analytes into the coating [27] as well as the partition coefficients. The effect of temperature in the extraction yield was investigated using the selected fibers in the range of 25 and 90 °C at a constant extraction time of 45 min. The maximum extraction efficiency was observed at 90 °C for both compounds due to the increase in the diffusion rate as equilibrium had not been reached [23,28].

3.3. Extraction time

In the direct SPME procedure, the detector response for the PA fiber, is proportional to the absorption, for the first 75 min for all the analytes, reaching a plateau after that time (Fig. 2a). For the PDMS fiber, the equilibration time of the analytes is shorter and almost reached after 45 min (Fig. 2a). As the PDMS coating is a viscous liquid polymer the diffusion coefficient of the analyte is orders of magnitude higher than its respective coefficient in a solid polymer.

The exposure time profiles of both analytes in the headspace sampling were also examined (Fig. 2b) since the fiber absorption of the analytes in the air is different from the absorption in the water. As expected, the equilibration time for both analytes reduced in the headspace sampling compared to the

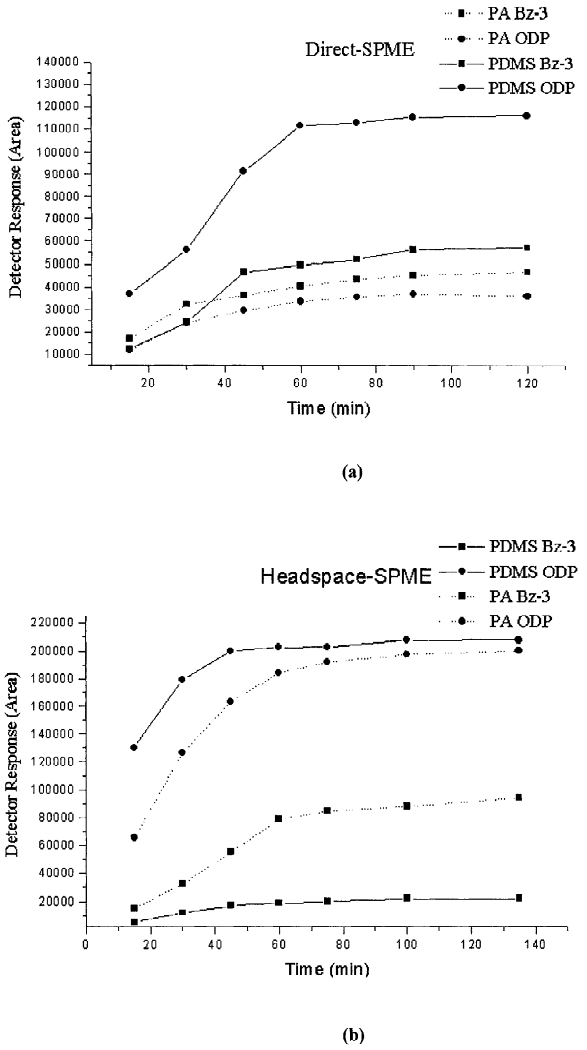


Fig. 2. (a) Detector response area vs. extraction time for benzophenone-3 and octyldimethyl-PABA in the direct SPME mode. (b) Detector response area vs. extraction time for 2-hydroxy-4-methoxybenzophenone and octyldimethyl-PABA in the headspace SPME mode. Concentration = 100 μg/l of each analyte; desorption temperature = 240 °C; desorption time = 8 min.

direct mode. Equilibrium times of 45 and 60 min were attained with the PDMS and PA coating, respectively. Reasonably, since the diffusion of analytes in the vapor phase is higher compared to the aqueous phase the equilibrium is achieved more rapidly [27].

For quantitative analysis, it is not necessary for the analytes to reach equilibrium as long as the extractions are carefully timed and the mixing conditions and sample volume remain constant [29,30]. Therefore, a moderate absorption time of 45 min was selected for the subsequent analysis, taking into consideration that the extraction efficiency was sufficient at this time [31]. Moreover, this sampling time was similar to the chromatography run time, thus allowing us to achieve a maximum sample throughput.

3.4. Salting out effect

Adding salts to aqueous solutions prior to SPME analysis has proven to change the extraction efficiencies due to change in the solvation environment. Moreover, the salt content of seawater is approximately 35 g/l, so the examination of its effect is relevant to this context. Salt addition up to 10 g/l NaCl resulted in an increase in the signal of Bz-3 in the DI-SPME with both fibers but extraction efficiency decreased at higher concentrations (Fig. 3). The salting out effect was more pronounced in the case of PA 85 μm while for PABA the addition of even small amounts of NaCl dramatically deteriorated its extraction possibly due to reduction of the diffusion rate of the analytes towards the fiber [32,33].

An increase in the extraction efficiency with increasing ionic strength (as NaCl) was observed in the case of headspace mode for both analytes. As can be seen in Fig. 3b, increasing ionic strength up to 30 g/l promotes the extraction of Bz-3 with both fibers while PABA response declines at salt concentration higher than 18 g/l. Nevertheless, 30 g/l NaCl was selected due to the higher extraction efficiency observed for 2-hydroxy-4-methoxybenzophenone, which exhibited the lower detector response in the HS mode.

3.5. Effect of pH

The effect of pH was investigated for its effect on the extraction of the tested analytes by both fibers in the direct mode employing phosphate buffer solutions in the pH range 1–10. The results depicted in Fig. 4 show that acidic conditions enhance the extraction of PABA. As PABA is a weak acid, the

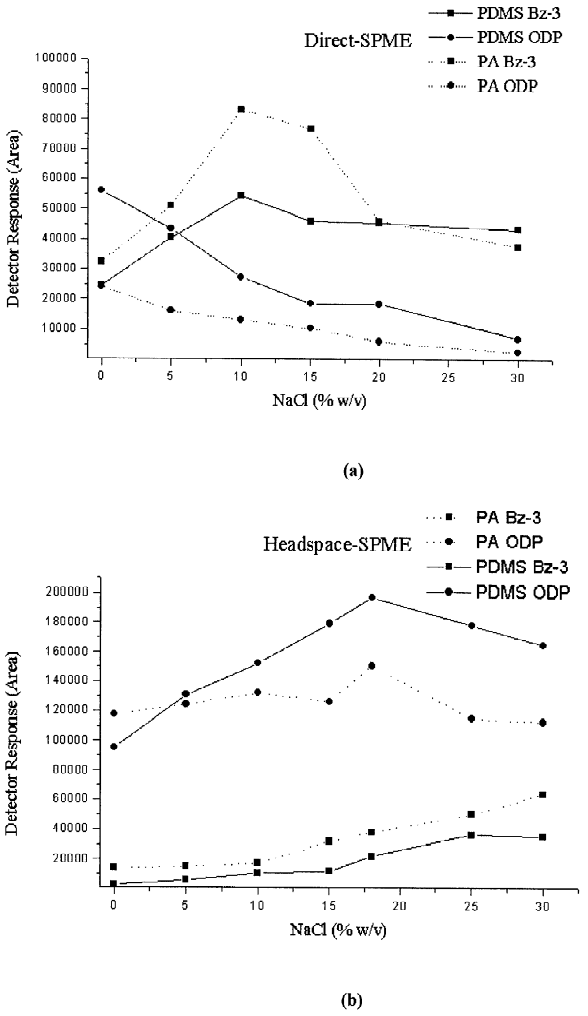


Fig. 3. (a) Influence of salt content on the detector response (area) for 2-hydroxy-4-methoxybenzophenone and octyldimethyl-PABA in the direct SPME mode. (b) Influence of sodium chloride on the detector response (area) for 2-hydroxy-4-methoxybenzophenone and octyldimethyl-PABA in the headspace SPME mode. Extraction time 45 min, other parameters as in Fig. 3.

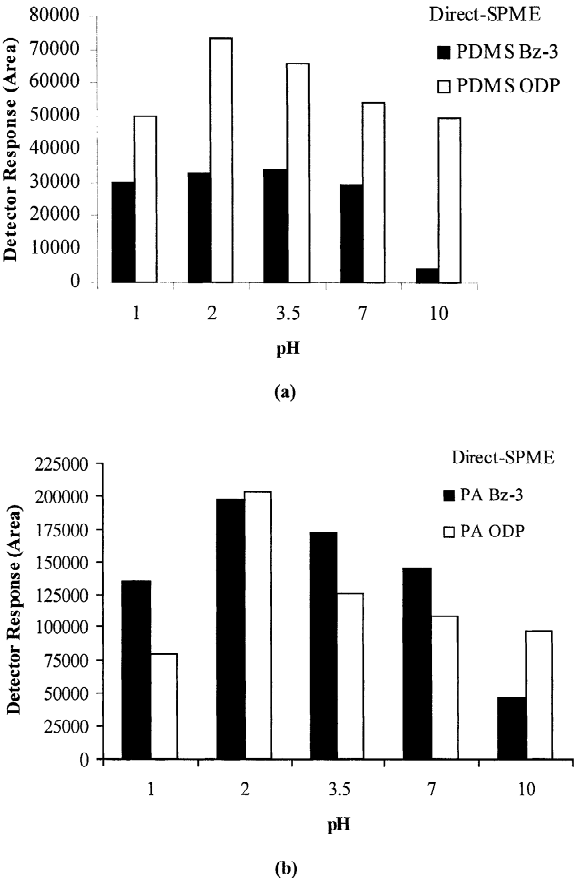


Fig. 4. Effect of pH on the detector response for 2-hydroxy-4-methoxybenzophenone and octyldimethyl-PABA in the direct SPME mode. No salt added, other parameters as in Fig. 3.

acid–base equilibrium shifts PABA toward its neutral form, which have a greater affinity for the fiber [34]. In the case of Bz-3 varying the pH from 1 to 7 had no significant adverse effect on the extracted amount by the PDMS fiber. At alkaline pH, the extraction efficiency for both compounds decreases dramatically (Fig. 4), possibly due to hydrolysis (possibly deprotonation) of both analytes in alkaline media. A similar pH pattern profile was also attained for the HS mode. The pH value of 2 was therefore employed throughout.

In concurrence with previous studies [29,34], the amount of analytes extracted was found to enhance in low pH and salt containing solutions (up to 10 g/l). For Bz-3, the enhancement factor was of about 1.2 while for PABA an increase 1.7 was observed. Based on the above results, a pH of 2 and salt of 10 g/l were employed for the analysis of real samples.

3.6. Figures of merit

The analytical characteristics of the proposed method were determined by properly designed experiments with the optimized direct and headspace

SPME protocol. Linear calibration curves in the range of 10 and 500 μg/l were generated by analyzing a series of eight concentration levels. Each solution was run in triplicate with both direct and headspace mode in the GC–FID and GC–MS systems. The quantitation limits (LOQs), defined as ten times the signal-to-noise ratio ($S/N=10$), were lower than 1.5 μg/l depending on the extraction mode, the detector's sensitivity and the target compound (Table 2). Compared to the existing methods were the determination of these compounds is usually feasible at the mg/l levels the presented results effort considerable improvement. From the results of Table 2 it is also revealed that the extraction of 2-hydroxy-4-methoxybenzophenone using the PA fiber is better than using the PDMS fiber with both extraction modes, primary due to the high polarity of PA coating. On the contrary, in the case of PABA the quantitation limits obtained with HS-SPME were lower than those obtained with DI-SPME. Quantitation of samples was made using calibration curves by plotting relative peak areas versus compound concentration. Each calibration level was prepared by spiking ultra pure water.

The precision of the methods was determined by analyzing five replicate spiked water samples consecutively at the concentration level of 50 μg/l. The precision expressed, as RSD values was lower than 9% with both detectors and for both analytes. Also, day-to-day precision was calculated over nine replicates (100 μg/l) analyzed in three different days in order to demonstrate procedure robustness. The RSD values obtained were 8 and 11% for 2-hydroxy-4-methoxybenzophenone and PABA, respectively.

Table 2
Analytical characteristics of the proposed approach

	GC–FID			GC–MS–SIM		
	Linearity[a] (R^2)	LOQ[b] (μg/l)	RSD[c] (%)	Linearity[a] (R^2)	LOQ[b] (μg/l)	RSD[c] (%)
DI-SPME (PDMS 100 μm)						
2-Hydroxy-4-methoxybenzophenone	0.994	1.70	6.7	0.995	2.47	8.2
Octyldimethyl-PABA	0.996	0.87	4.5	0.996	1.20	6.6
DI-SPME (PA 85 μm)						
2-Hydroxy-4-methoxybenzophenone	0.998	1.17	5.1	0.997	1.70	6.8
Octyldimethyl-PABA	0.994	2.47	5.8	0.996	2.93	8.7
HS-SPME (PDMS 100 μm)						
2-Hydroxy-4-methoxybenzophenone	0.992	4.10	7.9	0.991	4.43	8.9
Octyldimethyl-PABA	0.999	0.60	6.2	0.998	0.73	7.5
HS-SPME (PA 85 μm)						
2-Hydroxy-4-methoxybenzophenone	0.994	2.53	5.5	0.997	2.90	8.5
Octyldimethyl-PABA	0.997	2.23	6.3	0.999	3.03	7.8
SPE						
2-Hydroxy-4-methoxybenzophenone	0.996	3.33	7.6	0.997	7.33	8.2
Octyldimethyl-PABA	0.997	0.27	5.5	0.998	8.33	7.8

[a] Concentration range 10–500 μg/l.
[b] LOQ = limit of quantitation.
[c] RSD = relative standard deviation (mean of three replicate experiments, $C=50$ μg/l).

3.7. Recovery studies

Recovery studies to evaluate the percentage of analyte extracted from spiked swimming pool and seawater samples were conducted with both the direct and the headspace sampling procedures. The relative recovery that is determined as the peak area ratio of real sample and ultra pure water sample spiked with analytes at the same concentration level (instead of absolute recovery as used in exhaustive extraction procedures) was applied because SPME is a non-exhaustive extraction procedure. The recoveries obtained for all types of waters ranged between 82 and 98% for both analytes, revealing that both modes can successfully extract these sunscreens constituents from water samples. In this case, the relative standard deviations of the concentrations observed compared to those expected were satisfactory with values less than 8% (Table 3).

3.8. Analysis of real samples

The direct and headspace SPME procedures, as well as the SPE method as a reference technique, developed in the present study, were applied to several samples obtained from the coastal area and swimming pools from the region of Epirus (N.W. Greece). Additionally, samples from the waste pipes of showers near swimming pools were collected and analyzed for their content in the target species. All samples were initially analyzed using GC–MS in order to confirm the identity of the compounds. The quantification of the samples was carried out according to the procedure described previously and the concentrations of the detected analytes were obtained from an average value of three measurements. All measurements were initially made with the PDMS 100-μm fiber and in the direct mode. When one analyte was not detected an alternative extraction mode was applied based on the optimum extraction procedure for its individual compound as previously mentioned.

The analysis performed by GC–MS–FID confirmed the presence of Bz-3 and PABA in many of the cases examined. The corresponding chromatogram of a real sample obtained by SPME following the recommended procedure and using GC–FID is shown in Fig. 5. The results obtained (Table 4) indicate that the SPME technique can be successfully applied to sunscreen residue determination in real water samples without matrix interferences (evidenced by spiking of appropriate amounts from the respective analytes).

From an analytical standpoint no significant differences were observed between both methods and in comparison with a reference technique whenever the concentration of the analytes were within the established quantitation limits ($S/N=10$). In seawater samples the increased dilution rate and high salt content resulted in non-detectable concentration levels (Table 4). However, the sampling strategy is a critical parameter for the representative monitoring of these compounds. Reasonably, maximum concentration levels should be expected during the

Table 3
Mean relative recoveries (%) from the extraction of the selected compounds from uncontaminated spiked water samples by the proposed and a reference technique[a]

	DI-SPME		HS-SPME		SPE (reference technique)
	PDMS 100 μm	PA 85 μm	PDMS 100 μm	PA 85 μm	
Ionian Sea					
2-Hydroxy-4-methoxybenzophenone	97	99	91	94	94
Octyldimethyl-PABA	85	82	98	95	93
Swimming pool					
2-Hydroxy-4-methoxybenzophenone	95	99	89	90	97
Octyldimethyl-PABA	94	98	97	95	95

[a] Mean of three replicate measurements. Concentration spiked = 10 μg/l.

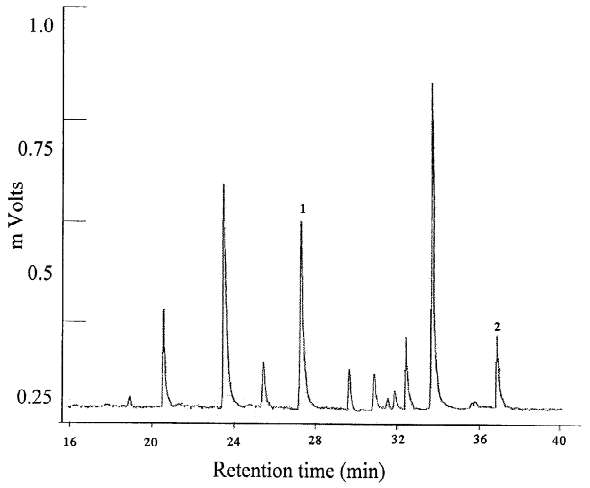


Fig. 5. A typical GC–FID chromatogram of 2-hydroxy-4-methoxybenzophenone and octyldimethyl-PABA obtained with the PDMS 100-μm fiber in the direct SPME mode from a contaminated swimming pool water sample: 1 = Bz-3, 2 = PABA.

maximum bathing activity depending also on the judiciousness of sunscreen application from the people undertaking these activities. At the earlier or later morning hours concentrations below the established quantitation limit were observed. This trend should also be expected for the swimming pool water samples in shorter time intervals (approximately 4–5 h) due to the water recirculation rates applied. Furthermore, from the results of Table 4 it can be seen that shower before using the swimming pool reduces the leaching of sunscreens to the pool water. On the contrary, in the game pool the concentrations were higher suggesting that compliance with the proposed guidelines during the sampling period was low.

Table 4
Sunscreens found in swimming pools, bathing waters (seawater) and shower waste samples collected throughout the Epirus region[a]

Sample	Concentration (μg/l)		Recovery (%)	
	Bz-3	PABA	Bz-3	PABA
Swimming pool 1	2.4[b]	n.d.[b,c]	98	94
Swimming pool 2 (Water game pool)	3.3[b]	2.1	96	95
Seawater	n.d.[b]	n.d.[b,c]	94	82
Shower wastes (pool 1)	9.9	6.2	98	92
Shower wastes (pool 2)	8.2	5.3	96	90

[a] All analysis were initially run with the PDMS 100-μm fibre in the DI mode. When necessary, additional measurements were performed and are given accordingly. Concentrations in μg/l.
[b] DI-SPME (PDMS 100 μm).
[c] HS-SPME (PA 85 μm).

4. Conclusions

An analytical methodology for the trace determination of two widely used sunscreen agents, 2-hydroxy-4-methoxybenzophenone and octyldimethyl-*p*-aminobenzoic acid, in water samples is presented for the first time. The method employs GC–MS or GC–FID detection with solid-phase microextraction. It was proven that the selected compounds could be efficiently determined under the optimized experimental conditions, while a case specific application (depending either on the matrix or on the target species) can further enhance the analytical utility of the proposed approach. The method was successfully applied for monitoring these sunscreen compounds in swimming pool and seawater samples at the μg/l levels.

Considering the latest efforts of the European Union for the update of the 76/160/EEC directive for bathing and swimming waters, this effort presents an initial analytical tool for the incorporation of sunscreen agent residuals in bathing water quality criteria for the first time.

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References

[1] C.G. Daugghton, T.A. Ternes, Environ. Health Perspect. 107 (1999) 907.
[2] M.E. Lindsey, M. Meyer, E. M Thurman, Anal. Chem. 73 (2001) 4640.

[3] A.W. Garrison, J.D. Pope, F.R. Allen, in: C.H. Keith (Ed.), Indentification and Analysis of Organic Pollutants in Water, Ann Arbor Science Publications, Ann Arbor, MI, 1976, p. 517.
[4] R. Hirsch, T. Ternes, K. Haberer, K.-L. Kratz, Sci. Total Environ. 225 (1999) 109.
[5] H.-R. Buser, T. Poiger, M.D. Müller, Environ. Sci. Technol. 32 (1998) 3449.
[6] T.A. Ternes, Water Res. 32 (1998) 3245.
[7] C. Potera, Environ. Health Perspect. 108 (2000) A446.
[8] B. Halling-Sorensen, S. Nors Nielsem, P.F. Lamdzky, F. Ingerslev, H.C. Holten Lutzhoft, S.E. Jorgensen, Chemosphere 36 (1998) 357.
[9] R.P. Stokes, B.L. Diffey, Br. J. Dermatol. 140 (1999) 259.
[10] M.W. Wright, S.T. Wright, R.F. Wagner, J. Am. Acad. Dermatol. 44 (2001) 781.
[11] T.A. Ternes, Trends Anal. Chem. 20 (2001) 419.
[12] R. Jiang, C.G.J. Hayden, R.J. Prankerd, M.S. Roberts, H.A.E. Benson, J. Chromatogr. B 682 (1996) 137.
[13] A. Chisvert, M.C. Pascual-Marti, A. Salvador, J. Chromatrogr. A 921 (2001) 207.
[14] S. Scalia, J. Chromatogr. A 870 (2000) 199.
[15] A. Chisvert, M.C. Pascual-Marti, A. Salvador, Fresenius J. Anal. Chem. 369 (2001) 638.
[16] A. Chisvert, A. Salvador, M.C. Pascual-Marti, Anal. Chim. Acta 428 (2001) 183.
[17] C.G. Tsiafoulis, M.I. Prodromidis, M.I. Karayannis, Anal. Chem. 74 (2002) 132.
[18] D. Lambropoulou, T. Sakellarides, T. Albanis, Fresenius J. Anal. Chem. 368 (2000) 616.
[19] M. Alpendurada de Fátima, J. Chromatogr. A 889 (2000) 3.
[20] Z. Zeng, W. Qui, Z. Huang, Anal. Chem. 73 (2001) 2429.
[21] D.A. Lambropoulou, T.A. Albanis, J. Chromatrogr. A 922 (2001) 243.
[22] D.A. Lambropoulou, I.K. Kostantinou, T.A. Albanis, J. Chromatrogr. A 893 (2000) 143.
[23] J. Pawliszyn, Solid Phase Microextraction: Theory and Practice, Wiley–VCH, New York, 1997.
[24] T. Felix, B.J. Hall, J.S. Brodbelt, Anal. Chim. Acta 371 (2001) 195.
[25] US National Institutes of Health, US National Toxicology Program (NTP) Technical Report, Toxicity Report Series Number 21, Technical Report on Toxicity Studies of 2-Hydroxy-4-methoxybenzophenone, US National Institutes of Health Publication No. 92-3344, NIH, Washington, DC, 1992, October.
[26] J.M. Allen, C.J. Gossett, S.K. Allen, Chem. Res. Toxicol. 9 (1996) 605.
[27] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843.
[28] Syracuse Research Corporation web site: http://esc.syrres-.com.
[29] K.D. Buchholz, J. Pawliszyn, Environ. Sci. Technol. 27 (1993) 2844.
[30] D.W. Potter, J. Pawliszyn, Environ. Sci. Technol. 28 (1994) 298.
[31] J. Ai, Anal. Chem. 69 (1997) 1230.
[32] L.H. Keith, W.G. Grummett, J. Deegan, R.A. Libby, J.K. Taylor, G. Wentler, Anal. Chem. 55 (1983) 2210.
[33] S.D. Huang, C.Y. Ting, C.S. Lin, J. Chromatogr. A 769 (1997) 239.
[34] L. Pan, M. Dams, J. Pawliszyn, Anal. Chem. 67 (1995) 4396.