Sample Preparation for Benzophenone Detection

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The benzophenones (BPs) constitute a group of compounds belonging to waterborne pollutants of emerging concern, which have been identified in the environment as well as in human fluids, such as urine, placenta, and breast milk, with the chemical formula $(C_6H_5)_2CO$ or Ph_2CO. They consist of two phenyl groups linked to a carbonyl group. Their accumulation and stability in the environment, combined with the revealed adverse effects on ecosystems including endocrine, reproductive, and other disorders, have triggered significant interest for research. Benzophenones should be extracted from environmental samples and determined for environmental-monitoring purposes to assess their presence and possible dangers. Numerous sample preparation methods for benzophenones in environmental matrices and industrial effluents have been proposed and their detection in more complex matrices, such as fish and sludges, has also been reported. These methods range from classical to more state-of-the-art methods, such as solid-phase extraction, dispersive SPE, LLE, SBSE, etc., and the analysis is mostly completed with liquid chromatography, using several detection modes.

benzophenones extraction environment analysis

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1. Introduction

The abundance of contaminants has already taken its toll on the environment and will continue to impact it and the ecosystems [1]. Given the severity of this issue, studies and reports are plentiful regarding their timely detection and measures for the prevention or remediation of contaminated environment [2][3]. Contaminants of emerging concern are not only understudied but also, there is no current legislation or regulation for some of them to restrict their usage [4]. Pharmaceuticals, laundry detergents, food additives, natural and synthetic hormones, pesticides, plasticizers, flame retardants, etc. [2][4], such as parabens [5], bisphenol A, 1,4-dioxane, as well as additives, and ingredients of personal care products, such as benzophenones (BPs), and many more are listed as waterborne pollutants of emerging concern [6]. They can be detected in urban, industrial, hospital, or agricultural wastewaters, entering the water cycle since they are discharged into the environmental compartments [7][8]. They are, mainly, produced by the use of commercial products or other activities and reflect the habits of modern society [6]. Even though their concentration levels in the environment are not high, their frequent occurrence and adverse impact on the environment make them important pollutants for research [9][10]. Over 700 contaminants of emerging concern, categorized into 20 classes, their metabolites, as well as their transformation products have been detected in the European marine environment [3].

It is easily understood that BPs constitute a class of compounds with a profound environmental impact. Therefore, their monitoring in the environment is of high importance. To this end, sensitive, rapid, and robust methods are needed, so as to obtain accurate results and introduce legislation for taking measures to avoid further environmental loading, safeguarding human health.

2. Solid-Phase Extraction

Solid-phase extraction (SPE) is one of the most exploited sample preparation methods for extracting and simultaneously preconcentrating and cleaning up samples from common interfering substances of the matrix. The SPE-based procedures have been developed as the basis for the development of new analytical methods. Archana et al. developed a procedure for the detection of common pharmaceuticals, personal care products, and BPs in river water [11]. For the extraction, a portion of the sample was passed through a C18 SPE cartridge (Agela Cleanert™ ODS C18, 500 mg/5 mL) and eluted, successively, with methanol and acetone/methanol 1:1. After evaporation, the sample was injected and analyzed with a high-performance liquid chromatography (HPLC) system, coupled to a diode array detector (DAD). Recoveries were found to be between 80% and 86%. This method has the edge of short time of analysis (15 min) and the good reproducibility (relative standard deviation (RSD) of intra-day and inter-day replicate analyses was 1.69% and 2.04%, respectively). However, the linear range was rather short (2–10 mg/L) compared with other methods [11]. In another work, Chiriac et al. compared two types of SPE cartridges, in order to determine the optimum for the detection of six BPs and to develop an analytical method [12]. The authors used Strata C18 cartridges, achieving recoveries between 81.9 and 96.4%, and Strata-X cartridges (pore size of 30μm, polymeric reverse phase), attaining somewhat lower recoveries (74.0–82.6%) [12]. The developed method achieved enrichment factors (EF) of 200 and 100 for surface water and wastewater, respectively. Despite the overall good characteristics, the method was time-consuming, given that 100-200 mL of sample was passed with a flow rate of 5 mL/min (20–40 min extraction time), plus 30 min of solvent evaporation was required [12]. Kharbouche et al. proposed the use of mesoporous silica-based materials MCM-41 and MCM-41-CN(a cyanopropyl derivatized MCM-41) as SPE sorbents, for the extraction of four BPs [13]. They optimized the parameters of the method and found that the optimum pH for MCM-41 was 6.0 and for MCM-41-CN was 3.5. Salinity proved to negatively affect the extraction of 4,4’-dihydroxybenzophenone (DHBP) and BP-1 since their recoveries were found to be below 55% from river water containing 0.12% salt. With regard to the sorbent amount, it was found that even 150 mg of MCM- 41 was not adequate to recover the polar DHBP (<30% recovery). On the contrary, 50 mg of the MCM-41-CN sorbent exhibited far better performance for all BPs. Using the MCM-41-CN as a sorbent, from 100 mL of sample spiked with 0.1 ng/mL of each BP, 74.8–106.4% recoveries were achieved along with an EF of 100. Quantification with the standard addition method revealed a matrix effect (ME) of 3.1–14.8% for the examined BPs. The intra-day precisions of the method were between 6.0 and 15.5 (spiked with 0.1 ng/L BPs) and from 8.2 to 10.8 (spiked with 0.5 ng/L). This hints towards a rather irreproducible method [13].

When the matrices to be analyzed are more complex, another cleanup step needs to be introduced to eliminate potential interferences. In their work, Wang and Kannan extracted BPs from wastewater and sludge from WWTPs and determined them [14]. Firstly, aliquots of water samples were separated from the suspended particulate matter, and then they were loaded on SPE cartridges, eluted with methanol and concentrated to a final volume using a nitrogen stream. For the sludge sample, an additional step of solid–liquid extraction was needed before applying SPE. Briefly, after freeze-drying of samples, the analytes were extracted with methanol/water (5:3) and after centrifugation and concentration, they were acidified with 0.2% formic acid prior to undergoing the above SPE procedure. The suspended particulate matter followed the same procedure as in sludge samples. The two extractions were enough to sufficiently extract the BPs from the sludge sample. The absolute recoveries of BPs were found in the ranges of 84–105%, 99–108%, and 81–122% for sludge, suspended particulate matter, and wastewater, respectively. It is noteworthy that this is the only work reporting the analysis of suspended particulate matter from the samples, at particularly low LOQs (0.25–0.50 ng/g) [14]. In relation to more complex matrices, Han et al. used animal and vegetation seafood as substrate for BPs detection using pressurized liquid extraction, a fast and green method for extraction, followed by a cleanup step with a mixed-mode cationic exchange SPE step for the removal of co-extracted compounds [15]. A mixed-mode cationic exchange was chosen over lipophilic balance and C-18 SPE, as recoveries for all BPs were superior. Additionally, after a comparison of the pressurized liquid extraction with Soxhlet and ultrasound-assisted methods, the recoveries were proved to be better with the pressurized liquid extraction (90.6–107.8%) compared with 83.5–88.7% and 81.4–85.2% for the other two methods, respectively [15]. Another SPE method using Oasis cartridges packed with 100 mg HLB sorbent was proposed by Luki et al. to preconcentrate and detect four BPs [16]. The working parameters were optimized by an experimental design which revealed that the elution solvent and percentage of methanol and pH were the influencing factors. In their work, Cadena-Aizaga et al. used an SPE method to extract eight organic UV filters, including BP-3, from seawater and wastewater samples [17]. The pH was adjusted to acidic values with formic acid and C18 cartridges were used, in the absence of salt. The best eluent and pH were MeOH:ACN (1:1, *v/v*), pH = 3 for seawater and MeOH, and pH = 7 for the wastewater, thus achieving preconcentration factors of 140 and 50, respectively. **Table 1** summarizes the features of relevant sample pretreatment methods based on SPE.

Table 1. Sample preparation methods based on SPE procedures for BP detection.

Method	Sample	Sorbent	Analytical Technique	BPs	Time for Treatment)	LOD (ng/L)	Recoveries % (RSD%)	Reference
SPE and MEPS	Groundwater, river	SPE(C-18) MEPS (syringe packed with C-18)	GC-MS	BP-1, BP-3, BP-8	-	34–67	96–107	[18]
					10	1800–3200		
SPE	River	MCM-41/ MCM-41-CN	UHPLC–MS	BP-1, DHBP, 4-OH-BP	~20 (3 days for synthesis)		74.8–106.4	[13]
On-line SPE	River Groundwater, effluent	cross-linked styrene/divinylbenzene polymer	LC-MS/MS	BP-3, BP-1, 4-OH-BP, DHBP, BP-8,	20	0.3–4	70–114	[19]

Method	Sample	Sorbent	Analytical Technique	BPs	Time for Treatment)	LOD (ng/L)	Recoveries % (RSD%)	Reference
				BP-2BP-4				
SPE	Surface water wastewater	C18	LC-MS/MS	2-OH-BP, 4-OH-BP, BP-2, BP-1, DHBP, BP-8	70 50	0.59–1.46 1.17–2.93	79-98	[12]
SPE Solid–liquid extraction	Sludge	methanol	HPLC-MS/MS	BP-3, 4-OH – BP, BP-1, BP-2, BP-8	~ 210	-	84–105	[14]
	suspended particulate matter				>210		99–108	
SPE	wastewater				~145		81–122	
SPE	River water	C18	RS-HPLC-DAD	BP	~120	1480	80–86	[11]
Pressurized liquid extraction and SPE	Seafood	C18	LC-QqLIT-MS/MS	BP-1, BP-2, BP-3	-	-	80.6–107.8	[15]
SPE	River water Tap water	Molecularly imprinted polymer	HPLC-DAD	BP-2, BP-1, BP-8, BP-6	~50 h (for synthesis) ~40 mins (for extraction)	250–720	86.9–103.3	[20]
SPE	Lake water	Oasis HLB 6 mL Vac Cartridges (100 mg sorbent)	LC-MS/MS	BP-1 BP-3 BP-4 4-OH-BP	280	0.04–4.4	62–82	[16]
SPE	Seawater	C18	UHPLC MS/MS	BP-3	-	11.3–36.4	43.3–100	[17]
	Wastewater					24.6–555.6	26.0–98.5	

LC-QqLIT-MS/MS: liquid chromatography–quadrupole linear ion trap–tandem mass spectrometry.

als used were specifically synthesized with high surface becoming more available to sorb the target analytes and were dispersed in the sample, providing ease of separation by centrifugation. In this context, Qiu and Ding synthesized zeolitic imidazolate framework-8 (ZIF-8) to extract BPs from surface, river, and seawater samples [21]. The ZIF-8 was prepared simply by grinding zinc oxide and 2-methylimidazole and then, mixing it with a small amount of deionized water. After optimization of the DSPE procedure, the synthesized material was added to the water samples, ultrasonicated, and centrifuged. To remove the BPs from the ZIF-8, methanol was used. The recoveries of BPs from real samples spiked with the BPs were found between 81.2 and 94.1% [21].

The sorbent used for a DPSE procedure can be a magnetic material, which simplifies its isolation from the solution just with the use of an external magnet. This procedure is also known as magnetic DSPE (mDSPE). Making use of this procedure, Piovesana et al. proposed a magnetic graphitized carbon black adsorbent, stable in water, to be used in an mDSPE [22]. To address the common problem of background contamination in trace detection of UV filters in the environment, solvent blanks were analyzed for every batch. Furthermore, procedural blanks and two spiked samples of the highest and lowest concentration of the calibration plot were analyzed. The authors claimed that the method was fast but the analysis time took more than 60 min, while no method optimization was carried out. So, a better overview of the parameters that affect the method is lacking [22]. **Table 2** summarizes the features of relevant sample pretreatment methods based on DSPE.

Table 2. Sample preparation methods based on DSPE and mDSPE procedures for BP detection.

Method	Sample	Sorbent	Analytical Technique	BPs	Time for Treatment (min)	LOD (ng/L)	Recoveries %	Reference
Magnetic DSPE	Lake water	Magnetic (Fe_3O_4)-graphitized carbon black (mGCB)	UHPLC-(QqQ) MS-MS	DHBP, BP4, BP-2, 4OH-BP, BP-1, BP-8, BP-3	~120 (2 days for synthesis)	1–5	85–114	[22]
Magnetic DμSPE	Swimming pool water	(Fe_3O_4@SiO_2@APTES@GO)	HPLC–(QqQ)MS/MS	4-OH-BP, BP-8, BP-3, BP-6, BP-1	~15 (4 days synthesis)	2500–8200	86–105	[23]
DSPE	Surface water River water Seawater	ZIF-8 + methanol	UHPLC-QTOF-MS	BP -3, BP-8, 2-OH-BP, 3-OH-BP, 4-OH-BP	~12 (~75 for synthesis)	0.1–7	81.2–94.1	[21]
MSPE	Soil	MOF-1210 (Zr/Cu)-Fe_3O_4 + 2% formic acid-acetonitrile	HPLC UV	BP-1, BP-3, BP-6	~62 (>4 days for synthesis)	10–20	87.6–113.8	[24]
DSPE Fixed Bed	Effluent from WWTP	Acetone—5%, formic acid, Fe-Cu nano	HPLC-DAD	BP-2, BP-6	~ 20 (~24 h for synthesis)	-	84–92	[25]
DPSE	River, swimming pool	CSMS@ polyaniline + Methanol	CE-MS/MS	BP-1, BP-2, BP-3,	~30 (>4 days for synthesis)	0.6–200	84.2–101.0	[26]

4. Liquid–Liquid Extraction

Method	Sample	Sorbent	Analytical Technique	BPs	Time for Treatment (min)	LOD (ng/L)	Recoveries %	Reference
	snow water domestic sewage	[27]		BP-6, BP-8, DHBP				

eveloped oled with s greater . Neither solvent volume nor methanol enhanced the recovery of BP-3 (<44%). It was speculated that either incomplete extraction from the matrix or transformation during the cleanup step was the main reason [27]. Only BP-3 was detected in the six Songhua River sediment samples (mean concentration: 0.38 ng/g of dry weight) and all BPs were detected in Saginaw and Detroit Rivers. Sludge from Northeastern China contained BP-3, BP-1, and 4-OH-BP.

Wang et al. proposed a dispersive liquid–liquid microextraction (DLLME) procedure, using a hydrophobic deep eutectic solvent (DES) that was formed in situ, when a hydrogen bond donor and acceptor were present [28]. BPs were extracted in the droplets of the DES, which could easily be collected after solidification/floating at 22 °C. This method is one of the most facile, fast, and green, as it consumes little to no organic solvent. Intra-day and inter-day precision values were 2.0–6.1% and 3.9–7.7%, respectively, making it one of the methods with the best repeatability and reproducibility. The extraction efficiency was not affected by any changes in the pH of the sample within the pH range of 2–10, avoiding the need for pH adjustment. Moreover, salinity was not found to affect the extraction procedure, thus, making it possible for application to samples with high salinity [28].

Another DES-based method was implemented by Wang et al. for an ultrasound-assisted DLLME [29]. The inter-day and intra-day RSD values were less than 5.9%, rendering it one of the most repeatable and reproducible methodologies, with EF values between 67 and 76. The optimum amount of DES used was 30 mg since greater partitioning of the BPs in the DES was recorded. By assisting the extraction procedure with ultrasounds, the high viscosity of the DES was not a problem, resulting in a 5 min extraction procedure. Concerning salt, it was found that the addition of 1% NaCl not only aided the extraction but also promoted phase separation. Increased salt concentrations (above 3%) resulted in increased viscosity of the solution, inhibiting the extraction by decreasing the diffusion rate and partitioning of BPs. By analyzing spiked river water samples, it was found that the ME was negligible in the proposed method.

Finally, using solidified droplets as the extracting phase, Zhang et al. used α−terpineol, a naturally occurring monoterpene enol, to extract 4 BPs from water samples. The EFs were between 29 and 47 and the recoveries ranged from 80.2% to 108.4%, with RSDs (intra- and inter-assay) less than 8.5%. [30]. The employment of α−terpineol provided a simple and rapid alternative for the determination of benzophenone compounds in aqueous samples. **Table 3** summarizes the features of relevant sample pretreatment methods based on LLE.

Table 3. Sample preparation methods based on LLE procedures for BP detection.

Method	Sample	Sorbent	Analytical Technique	BPs	Time for Treatment (min)	LOD (ng/L)	Recoveries %	Reference
DLLME	Water samples	Hydrophobic DES	HPLC-DAD	BP-1, BP-2, BP-3, BP-6	~10–15	600–1500	73.1 to 99.8	[28]
DES-ultrasound-assisted DLLME	River water	DES	HPLC-UV	BP-1, BP, BP-3	~10–15	150–300	90.2–103.5	[29]
LLE and SPE	Sediment	Methanol (LLE) oasis HLB (SPE)	LC-MS/MS	BP-3, BP-1, BP-8, BP-2, 4-OH-BP	~200	41–61	70–116	[27]
	Sewage sludge					0.41–0.67	38.3	
DLLME	Lake water Seawater	Magnetic in situ-formed IL	UHPLC-DAD	BP-1, BP-2, BP-3	5	12.3–20.0	68.0–92.5	[31]
LLE	Tap water Stream water Seawater	DEHPA + Fe_3O_4	HPLC-UV [33]	BP-1, 4-OH-BP, BP-3	~7	700–800	80–103	[32]
DLLME	Tap water River water Domestic wastewater Factory wastewater	α−terpineol	HPLC-DAD	4OH-BP BP-1 BP BP-4	~20	120–530	75–108.4	[30]

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the method does not exhibit as good LODs as other methods (329 ng/L), it shows that the fluorometric detection of BPs is also possible.

An extraction and simultaneous cleanup step assisted by ultrasound was proposed by Sánchez-Brunete et al. [34]. In this procedure, a glass column containing two circular 2 cm diameter filter papers was packed with anhydrous sodium sulphate and C18. Then, an amount of sieved sediment or soil sample was placed inside the column. The whole system was placed inside a sonication water bath supported by a tube rack. Through the formed packed column, a mixture of ethyl acetate:methanol (90:10, *v*/*v*) was passed, while sonicating, in order to extract the BPs and isolate them from the matrix. Although ethyl acetate eluted most of the BPs, the most polar ones such as BP-8 and BP-6 were better eluted by a 90:10, *v/v* ethyl acetate:methanol mixture. Matrix effects of up to 27% were nullified by the use of internal standard. The authors investigated the effect of moisture and found that it had no effect on the recoveries. Similarly, a residence time of 72 h between spiking and analysis had no effect on the recoveries. Furthermore, the RSD values of 3.4% to 7.5% for the intra-day precision indicated good repeatability [34]. Finally, as this method utilizes a GC-MS system for analysis, the low thermal stability and volatility of the BPs necessitate a derivatization step, thus complicating the procedure [34].

Modified stir bars can also be used for BP absorption. Merib et al. created a cork-powder-coated polypropylene fiber material for stir bars, which was used for bar adsorptive microextraction (BAmE) of BP from aqueous samples [35]. The authors reported the optimal extraction time for BP to be 90 min. They opted for a 120 min extraction time as a middle ground for BP, triclocarban, and paraben extraction. For the purpose of this review, the 90 min extraction time for BP is further discussed. In this framework, not only the extraction step is time-consuming but also the 30 min desorption time adds up to the already time-consuming procedure. In a positive light, the BAmE procedure needs low extracting solvent when compared to traditional SPE, eliminating the need for laborious evaporation under a nitrogen stream. It is noteworthy that as the bar operated well below its saturation point, the authors found that by decreasing the bar length to half and by increasing the desorption volume by 2.5 times, they could improve the LOD by 2.5 times [35].

In the study of Celeiro et al., three coated sol–gel fabric phases, i.e., nonpolar, medium-polar, and polar, were fabricated and compared [36]. The highest extraction of BPs was achieved with the non-polar poly-dimethylsiloxane coating. A major drawback of poly-dimethylsiloxane coating in regular SPE is that it is highly viscous, hindering the analyte migration and increasing the sorption time. The sol–gel coating resulted in a thin film that was finely integrated into a silica fabric phase. The substrate aided the extraction by bringing the analytes close to the sorbent to interact with various interactions. With the proposed sorbent material, only 20 min are needed for the extraction. On top of that, high reproducibility of the synthesis and analysis were recorded. Although this study detected UV filters in real samples, BP-3 was not one of them [36].

Huang et al. in their novel work, developed a Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method to extract ten different BPs from fish samples and compared the developed method with an SPE one [37]. For the QuEChеRS method, the use of ACN with 1% acetic acid, anhydrous $MgSO_4$, NaCl, Sepra C18-e (50 μm, 65 Å), and Superclean primary secondary amine was proposed after optimization. At first, they tested the use of DSPE-enhanced matrix removal for the fish samples with lipid content higher than 5% but it seemed to decrease the recovery of the BPs. They also tested an SPE extraction method with PRiME HLB and SPE-C18 cartridges, but the extraction results were lower than those with QuEChеRS method, with recoveries between 55% and 154%. The repeatability and reproducibility of the method were remarkably low, with RSDs reaching 26.6% and 29.3%, respectively, for the detection of the BPs [37]. This method showed that the detection and extraction of BPs are possible even with complex matrices, such as fish but further optimization is needed to increase its repeatability and reproducibility. **Table 4** tabulates the most important features of the above sample pretreatment methods.

Table 4. Sample pretreatment methods not falling into the pretreatment modes of **Table 1**, **Table 2** and **Table 3** for BP detection.

Method	Sample	Sorbent	Analytical technique	BPs	Time for Treatment (min)	LOD (ng/L)	Recoveries %	Reference
BAmE	Aqueous samples	15 mm—cork-powder-coated polypropylene hollow fibers	HPLC-DAD	BP	120 (15 h for synthesis)	500	100%	[35]
		7.5 mm (half bar)—cork-powder-coated polypropylene hollow fibers				200	123%	
SBSE	Soil	COF-V polypropylene hollow fibers	HPLC-UV	BP-1, BP-3, BP-6, Ph-BP	210–240 (100 h for synthesis)	20–30	73.9–111.7	[38]
BAmE	Seawater wastewater	P2-polymer-coated stir bar	HPLC–DAD	BP, BP-3, BP-1, 4-OH-BP	~260	300–500	76.6–103.5	[39]
FPSE	Lake water River water Seawater	Sol–gel-coated sorbent	FPSE-GC/MS	BP-3	20	4.5	94	[36]
QuEChERS	Fish samples (<5% lipids)	$MgSO_4$ PSA + Methanol	UHPLC–MS/MS	BP, BP-1, BP-2 BP-3, BP-8, 4-OHBP	~100	0.001–0.122	70–166	[37]
	Fish samples (>5% lipids)						74–182	
Zn-Tb CP	-	CP	Fluorescence	BP	~30 (~96 h for synthesis)	-		[33]
Solid–liquid extraction	Soil	ethyl acetate–methanol	GC-MS	BP-1, BP-3,	~105	0.07–0.10	Soil 89.8–	[34]

Method	Sample	Sorbent	Analytical technique	BPs	Time for Treatment (min)	LOD (ng/L)	Recoveries %	Reference
and SPE		(90%–10%), C18 + anhydrous sodium sulphate		BP-6, BP-8, 4-OH-BP			104.4	
	Sediment					0.14–0.28	Sediment 88.4–105.3	
Ultrasound-assisted Solid–liquid extraction	Soils	methanol	UHPLC-MS	BP-1, BP-2, BP-3, BP-6, BP-8	~60	0.05–0.40	83–107	[40]
	Wastewater treatment plant compost					0.06–0.30		

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