



Development of an analytical method based on derivatisation solid-phase microextraction combined with gas chromatography-mass spectrometry for the determination of bisphenol analogues in environmental waters

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ABSTRACT

Bisphenol analogues, including bisphenol A (BPA), are pervasive environmental contaminants known for their endocrine-disrupting properties. With the increasing use of alternative bisphenols due to regulatory restrictions on BPA, monitoring their presence in aquatic systems is critical. However, their low concentrations in environmental matrices complicate their detection. This study presents the optimisation using an experimental design of a solid phase-microextraction (SPME) method, coupled with gas chromatography-mass spectrometry (GC-MS), for the determination of nine bisphenols analogues (BPA, BPAF, BPF, BPE, BPG, BPB, BPZ, BPZ, and BPC2) in drinking water, environmental waters, and wastewater samples. Acetylation was used as a derivatisation technique to improve the analytes' volatility and stability.

The optimized method comprises the extraction of 15 mL of water by DVB/CAR/PDMS fibre in direction immersion mode adding 50 μL of acetic anhydride. The temperature was 100 $^{\circ}\text{C}$ and the extraction time 30 min. Method validation demonstrated excellent linearity ($R^2 > 0.999$), low detection limits in the low $\mu\text{g L}^{-1}$ range, and general recoveries above 80 % in real samples. The application to 19 water samples revealed the presence of seven bisphenols analogues reaching up to 3.4 $\mu\text{g L}^{-1}$, with BPE detected at the highest concentrations and BPA as the most frequently detected compound. This method provides a sensitive, efficient, and environmentally sustainable approach for the analysis of bisphenols in complex water matrices, aligning with green chemistry principles.

1. Introduction

Bisphenols (BPs) are widely utilised as additives across numerous industries, such as plastic packaging, electronics, medical equipment and composites materials [1]. Bisphenol A (BPA) and its analogues including BPAF, BPAP, BPB, BPF, BPS, and BPP, constitute a class of structurally related chemicals characterized by two phenolic rings connected by a bridging carbon atom or alternative linkages [2,3]. BPA is the most extensively produced and used bisphenol analogue globally, with China being the leading contributor to the global market, accounting for approximately 3.3 million tonnes of BPA consumption in 2022 [4]. BPA is recognised as an endocrine-disrupting chemical (EDC) and has been linked to numerous adverse health effects, including diabetes, cardiovascular disease, reproductive disorders, breast cancer and

birth effects [5,6]. Growing concerns regarding widespread human exposure and its potential health impacts have prompted the implementation of regulations on BPA production and use. The U.S. Environmental Protection Agency (EPA) is continuing to evaluate BPA and its alternatives under the Toxic Substance Control Act (TSCA) to determine their safety profiles [7]. Regulatory agencies such as European Chemicals Agency (ECHA) have proposed restrictions under the REACH regulations on BPA and certain analogues, emphasising precautionary measures due to their endocrine disrupting potential [8]. In 2011, the European Union prohibited the use of BPA in infant feeding bottles [9]. Likewise, in 2010, Canada banned the importation and sale of polycarbonate bottles containing BPA [10]. Regarding the regulations in water, the European Drinking Water Directive, from 12 January 2026, water suppliers will be required to meet a maximum BPA concentration

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of $2.5 \mu\text{g L}^{-1}$ [11].

Growing public concerns and regulatory restrictions on BPA have recently encouraged the production and use of BP analogues as substitutes for BPA in a range of applications [12,13]. Alternative bisphenols were initially considered less toxic than BPA. However, recent evidence suggests that BPAF, BPF, BPB, BPS, and tetramethyl bisphenol F (TMBPF) may exert adverse effects that are comparable to or even greater than those of BPA [14–17]. Given their harmful effects on humans and wildlife including genotoxicity, estrogenicity, cytotoxicity, and carcinogenicity, these compounds have been classified as contaminants of emerging concern [18].

Due to their extensive use in essential applications ranging from electronics to food packaging, substantial quantities of these chemicals have been released into the aquatic environment [19]. BPA can migrate from resins or polymeric materials into water or food when exposed to elevated temperatures. Consequently, the likelihood of BPA contamination in these matrices is considerable, given the widespread consumption of drinking water and canned foods globally [20]. Because BPs are typically present at very low levels in water and food samples, directly detecting them is difficult, and therefore sample preparation methods with high sensitivity and selectivity are essential to effectively extract and concentrate these compounds while simultaneously eliminating major interferences before the instrumental analysis [21].

Traditional methods tend to be labour-intensive and time taking, consuming large amounts of both samples and organic solvents, as multiple extraction steps are usually required to achieve complete isolation of various BPs. The extensive use of organic solvents contribute to environmental pollution, poses health risk, and incurs additional costs for waste treatment [22]. Consequently, in recent years, modern and miniaturised extraction techniques have been adopted, enabling reductions in sample and solvent volumes, minimising waste generation, and aligning with the principles of ‘Green Chemistry’. Different sample preparation techniques both conventional and modern such as solid-phase extraction (SPE) [12,13, 23–26], ultrasound-assisted extraction (UAE) [27], dispersive liquid-liquid microextraction (DLLME) [28], and liquid-liquid extraction (LLE) [29], have been reported in the literature for extracting BPs from various types of water matrices of environmental concerns. Solid-phase microextraction (SPME) represents an effective alternative to conventional methods, as it provides a solvent-free and more environmentally sustainable alternative to previously described procedures. Moreover, SPME generally yields a high enrichment factor, shortens extraction time, and can be easily automated, facilitating high sample throughput [30].

Advances in instrumental technologies, particularly chromatographic techniques like liquid chromatography (LC) and gas chromatography (GC) chosen according to the chemical properties of the target compounds and their coupling with mass spectrometry (MS) or tandem mass spectrometry (MS/MS), have been extensively applied in the analysis of BPs. Nevertheless, effective sample preparation remains essential, as it enables the extraction, pre-concentration, and clean-up of analytes from complex matrices, thereby improving method sensitivity and prolonging instrument lifespan. Since BP analogue generally exhibit low volatility, derivatisation is required to enhance their volatility prior to GC–MS analysis [31–33]. The integration of SPME with GC–MS offers a powerful analytical approach, and SPME is therefore considered a promising technique for extracting BPs from environmental water samples.

This study seeks to establish a rapid, sensitive, and selective approach for analysing BP compounds in drinking waters, environmental waters, and wastewater samples using *in-vial* derivatisation SPME, without relying on organic solvents, and combined with GC–MS detection in selected ion monitoring mode (GC-MS-SIM). Linearity, precision, and detection limits were assessed to evaluate the optimised method, intended for the analysis of these compounds in water samples collected from various locations in Spain and Portugal. To the best of our knowledge, this is the first reported SPME-GC–MS method employing

simultaneous *in-vial* acetylation for the analysis of these compounds in environmental waters.

2. Experimental

2.1. Chemicals and materials

A standard mixture containing BPs (BPAF, BPF, BPE, BPA, BPG, BPC2, BPZ, and BPM), each at a concentration of $2000 \mu\text{g mL}^{-1}$ in acetone, was sourced from LGC Standards Ltd. (Barcelona, Spain) with a minimum purity of 98 %. BPB (97.5 %) was purchased from TargetMol (Boston, USA). Acetic anhydride, used as the derivatising agent, was obtained from Merck (Darmstadt, Germany), whereas N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA, 99 %) containing 1 % trimethylchlorosilane (TMCS) was procured from Supelco (Bellefonte, PA, USA). Pyridine (99.8 %) was provided by Sigma-Aldrich. Methanol and ethyl acetate were purchased from Fluka Analytical (Steinheim, Germany), while ultrapure water (MS-grade water) was acquired from Scharlab (Barcelona, Spain). Sodium chloride (NaCl) was obtained from Panreac (Barcelona, Spain), and sodium bicarbonate (NaHCO_3 ; 99.0–100.5 %) from Glentham Life Sciences Ltd. (SN13 9SW, United Kingdom). All chemicals and solvents used were of analytical grade.

Commercially available SPME fibres, 50/30 μm divinylbenzene-carboxen-polydimethylsiloxane (DVB/CAR/PDMS), 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane-divinylbenzene (PDMS/DVB), and 85 μm polyacrylate (PA), mounted in manual holders, were obtained from Supelco (Bellefonte, PA, USA). Prior to use, the fibres were prepared according to the provided guidelines by placing them into the GC–MS injection port under a continuous carrier gas flow, with DVB/CAR/PDMS at 270 °C for 1 hour, PDMS/DVB maintained at 250 °C for 30 min, PA at 280 °C for 1 hour, and PDMS at 250 °C for 1 hour. A stock solution containing all the BP standards was prepared in methanol. Working solutions were subsequently prepared and stored at $-20 \text{ }^\circ\text{C}$.

2.2. Sampling sites and sample collection

Various real water samples were obtained from locations in Galicia (NW Spain) and Porto (Portugal): river water, seawater, wastewater, port water, artificial turf crumb rubber football field irrigation water, tap water, spring water and swimming pool water. All these samples were collected (30 mL - 1 L) in glass vials or bottles, transported and stored at $-20 \text{ }^\circ\text{C}$ in the dark. Further details of the real samples are provided in Table S1.

2.3. Solid-phase microextraction procedure

Following the optimised experimental conditions (see Results and Discussion), 15 mL of water samples were placed in 20 mL vials. To perform *in-vial* derivatisation, 100 mg of NaHCO_3 and 50 μL of acetic anhydride were introduced into the mixture. The vials were sealed with aluminium caps fitted with PTFE-faced septa and placed in a water bath maintained at 100 °C. After 5 min to allow the sample to reach a steady state, the SPME fibre (DVB/CAR/PDMS) was inserted directly into the sample (DI-SPME) and exposed for 30 min. The samples were continuously stirred throughout the extraction employing a magnetic stirrer plate (Agimatic-N with heating, J.P. SELECTA®), and a magnetic bar. After extraction, the fibre was retracted into the SPME holder needle, transferred to the GC injection port, and thermally desorbed for 5 min at 270 °C.

Ultrapure water standards were prepared by spiking with the target compounds to obtain various concentrations and analysed using the aforementioned SPME procedure. To avoid false-positive results, fibre blanks and procedural blanks using 15 mL of ultrapure water were carried out each day.

2.4. GC–MS analysis

Analyses were conducted on an Agilent 7890A gas chromatography coupled to an Agilent 5975C inert mass selective detector featuring a triple-axis detector, alongside an Agilent 7693 autosampler (Agilent Technologies, Palo Alto; CA, USA). A ZB-Semivolatiles column (30 m × 0.25 mm × 0.25 μm) from Phenomenex (Torrance, CA, USA) was employed for chromatographic separation. High purity helium (99.999 %) served as the carrier gas at a flow rate of 1.0 mL min⁻¹. The oven temperature programme began at 80 °C (held for 1 min) to 210 °C (held for 2 min) at 15 °C min⁻¹, and then to 280 °C (held for 1 min) at 3 °C min⁻¹, with a total run time of 34 min. The injection volume was 1 μL for the organic solvent standards, and was performed in pulsed splitless mode (1 min at 75 mL min⁻¹) at temperature of 260 °C. The transfer line, ion source and quadrupole were maintained at temperatures of 290, 150, and 300 °C, respectively. Compounds were examined in selected ion monitoring (SIM) mode, as summarised in **Table S2**.

2.5. Statistical analysis

Descriptive and basic statistical analyses, as well as evaluation of the experimental design, were carried out using the Statgraphics Centurion XIX software package (Manugistics, Rockville, MD, USA). A factorial design was selected to optimise the extraction step by assessing the experimental parameters, including the interaction effects among factors. The greenness and practicability of the proposed method were evaluated with the AGREEP and the BAGI (Blue Applicability Grade Index) softwares. All calculations for method validation were performed using Microsoft Excel.

3. Results and discussion

3.1. Method optimisation

The GC method was optimised by systematically assessing various instrumental parameters, including the oven temperatures gradient, injection mode, injection volume, and carrier gas flow rate. The optimised conditions detailed in **Section 2.4** (GC–MS analysis) yielded better sensitivity and selectivity while reducing the total analysis time.

3.2. Selection of derivatising agent

In the preliminary experiments, both silylation and acetylation of the target analytes were evaluated. Given the presence of an active hydrogen atom in the -OH groups of these molecules, such derivatisation approaches are considered appropriate. As bisphenol analogues typically exhibit low volatility, derivatisation is required to enhance their volatility prior to GC–MS analysis [34].

For acetylation, BP standard solution in ethyl acetate were treated with 10 μL of pyridine and 60 μL of acetic anhydride, and incubated at 60 °C for 60 min. In the silylation approach, the same volume (60 μL) of the silylating reagent BSTFA was used under identical time and temperature conditions. Both derivatisation approaches yielded comparable chromatographic quality with higher sensitivity and better chromatographic peak shapes for all the compounds, in comparison to the non-derivatised BPs, some of them not even detected without derivatisation. Silylation produced slightly higher responses. However, this procedure cannot be carried out in water [35].

Generally, silylation needs temperature control, a time to complete the process, and an anhydrous medium while acetylation can occur in water, which valued a green solvent [29]. Besides, the derivatising reagent for silylation is more toxic and expensive than acetic anhydride. In addition, some byproducts may be produced under silylation due to the elevated reaction temperature [36]. Given these conditions and the goal of studying bisphenol compounds in various water samples acetylation was selected as the preferred derivatisation method.

3.3. Optimisation of the SPME extraction process

The sensitivity of the SPME extraction technique is predominantly influenced by the distribution constant of the analytes between the sample matrix and the fibre material. It is crucial to consider not only the individual effects of the factors that influence the extraction, but also the interaction effects between them. Accordingly, optimisation was conducted to determine both the relevant factors and their optimal levels, considering a multivariate experimental design. The fibre coating constitutes one of the most critical parameters, as the extraction efficiency of the target compounds depends on their affinity for the fibre material. To identify the most suitable fibres to include in the experimental design, preliminary tests were carried out using DVB, PA, CAR/PDMS/DVB, and PDMS/DVB fibres. These experiments were performed with 15 mL of ultrapure water spiked to 0.1 μg L⁻¹ of the compounds, with the addition of 100 mg NaHCO₃ and 200 μL acetic anhydride, under immersion mode at 100 °C for 30 min. The results are presented in **Fig. 1a**. Among these, the DVB/CAR/PDMS fibre exhibited the highest extraction efficiency for the majority of the target BP compounds, followed by PDMS. Both were selected for further optimisation.

The extraction mode is another key parameter in SPME. Both headspace (HS) and direct immersion (DI) modes were evaluated using the most appropriate fibres, DVB/CAR/PDMS and PDMS. Experiments were carried out under the same conditions as previously described. The results for the DVB/CAR/PDMS fibres are shown in **Fig. 1b** As illustrated, higher responses were observed using the DI mode for all compounds, which can be attributed to the direct contact of the fibre with the sample, enhancing the transfer of analytes. Conversely, several compounds were not detected when HS mode was applied.

The efficiency of SPME depends on several factors, and when the extraction is combined with *in situ* derivatisation, the yield of derivatisation also affects the overall process. In addition to the fibre coating, the extraction mode, the volume of the derivatising agent acetic anhydride and amount of NaHCO₃, and the extraction temperature should be studied. The addition of salt (NaCl), might improve extraction by raising the ionic strength of the solution, thereby reducing the solubility of organic compounds in water and facilitating their transfer to the fibre. However, this effect can vary depending on the analytes' polarity and molecular weight. Both presence and absence of NaCl were tested to determine its role in enhancing or inhibiting extraction efficiency. Another important factor was the quantity of NaHCO₃, which was added to buffer the pH and assist in the *in-vial* derivatisation process. Alongside this, the volume of acetic anhydride, the chosen derivatising agent, was varied to identify the amount that ensured extensive derivatisation. All experiments were performed at elevated temperatures (up to 100 °C) to facilitate both derivatisation and analyte transfer into the fibre and stirring was applied to reduce equilibrium time and enhance analyte fibre contact [37–38].

A screening factorial design was employed to simultaneously evaluate the effects of the five aforementioned factors. The addition of salt (Factor A) was tested at two levels (0 and 30 % w/v), the volume of the acetic anhydride (Factor B) at 50 and 200 μL, the amount of NaHCO₃ (Factor C) at 50 and 100 mg, the temperature (Factor D) at 60 and 100 °C, and the type of fibre (Factor E), using DVB/CAR/PDMS and PDMS. These factors, summarised in **Table 1**, were investigated using a 2⁵⁻¹ factorial design, resulting in 18 experiments, with one additional included for a total of 19 experiments. All experiments (*n* = 2) were performed using 15 mL of ultrapure water spiked at 5 μg L⁻¹ with the target compounds, at 100 °C for 30 min.

The analysis of variance (ANOVA), summarised in **Table 2**, illustrates the effects of the examined factors on the responses. The F-ratio reflects to which each factor and their interactions contribute to the variance of the response, while the p-values indicate the statistical significance of these effects. Factors or interaction with p-values < 0.05 are considered statistically significant at the 95 % confidence level. As shown, the salting-out effect adding NaCl (%) and the fibre type were significant for

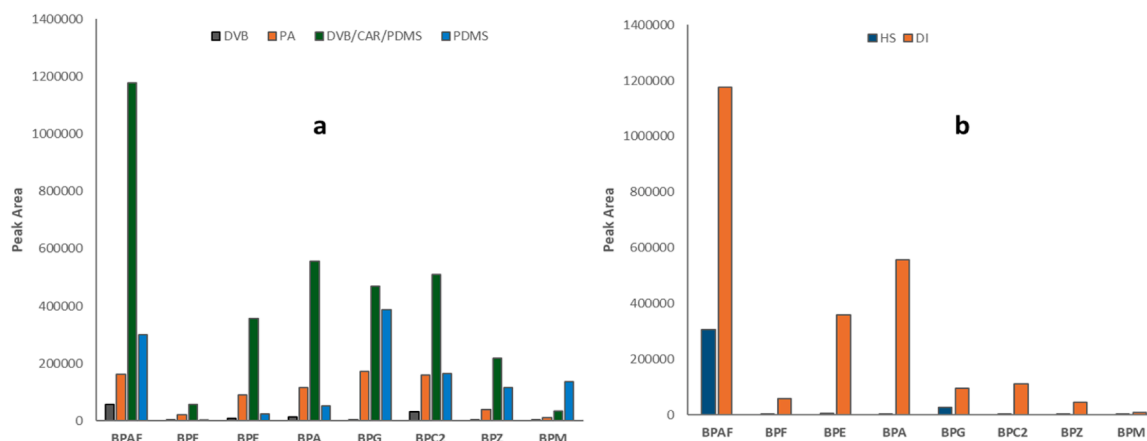


Fig. 1. (a) Influence of fibre coatings in the extraction efficiency (responses for the last 4 compounds have been multiplied by 5 to facilitate visualisation) and (b) extraction mode HS vs DI.

Table 1

Experimental factors and levels in the experimental design.

Factors	Code	Low (-)	High (+)	Units	Continuous
NaCl	A	0	30	%	Yes
AA*	B	50	200	μL	Yes
NaHCO ₃	C	50	100	mg	Yes
Temperature	D	60	100	$^{\circ}\text{C}$	Yes
Fibre	E	DVB/CAR/PDMS	PDMS		No

* Acetic anhydride.

most of the compounds, as was the interaction between these two factors (AE). Temperature was significant for certain compounds, whereas the remaining factors generally did not show significant effects.

Fig. 2a graphically shows the influence of the factors through the pareto charts and Fig. 2b including the main effects plots for some selected compounds. As commented, the fibre coating (D) resulted statistically significant for most of the compounds (BPF, BPE, BPA, BPG and BPM), being more favourable the use of the DVB/CAR/PDMS for all analytes. The salting-out effect (A) was significant showing different behaviour regarding the compounds. Analysing only the main factors (see Fig. 2b) for BPF, BPE, and BPA, the salt addition improved extraction whereas for BPG and BPM the behaviour was just the opposite. Nevertheless, the interaction between those factors is significant in most cases. AE interaction shows as in general the addition of salt benefits PDMS extraction but disfavours the extraction by the DVB/CAR/PDMS fibre, as can be seen in the interaction plots in Fig. 2c. Therefore, considering the more suitable fibre the addition of NaCl is not recommended. The temperature was also significant for 2 compounds but for all the targets higher temperature (100 $^{\circ}\text{C}$) achieved higher response. Regarding acetic anhydride and NaHCO₃, in general were not significant for any compound except for BPG for which 50 μL and 100 mg, respectively, were more suitable. To conclude, the selected SPME conditions extracted from this experimental design were: 0 % NaCl, 50 μL of acetic anhydride, 100 mg NaHCO₃, 100 $^{\circ}\text{C}$, and DVB/CAR/PDMS fibre.

3.4. Method performance evaluation

The method performance was evaluated in terms of linearity, limits of detection (LOD), limits of quantification (LOQ), precision, and accuracy. The results are presented in Table 3. Calibration was conducted using SPME under optimised conditions across a concentration range of 0.005 to 5 $\mu\text{g L}^{-1}$ for each analyte in ultrapure water, at seven levels with three replicates per level ($n = 3$). The method demonstrated a directly proportional relationship between the amount of compound and its chromatographic response, with determination coefficients (R^2) equal to

or greater than 0.999. Figure S1 shows a SPME-GC-MS chromatogram of a sample (ultrapure water spiked at 1 $\mu\text{g L}^{-1}$).

The LODs and LOQs were determined as the analyte concentration giving signal-to-noise (S/N) ratio of 3 and 10, respectively, using spiked samples at low concentrations level. The limits were below 0.005 $\mu\text{g L}^{-1}$ for most analytes. The instrumental precision was assessed within a day ($n = 3$) and across several days ($n = 6$) (Table 3).

Recovery studies were performed using four different real water matrices (spring, river, waste and seawater) spiked at 0.1 $\mu\text{g L}^{-1}$ with the nine BPs. In those cases where the compounds were initially detected in the samples, their responses were subtracted. Fig. 3 presents the results obtained for each of the water matrices. For the four real samples the recoveries for all compounds were satisfactory, ranging from 73 % to 120 %, as shown in Table S3. For BPG and BPM the initial recoveries were low (20 % and 47 %, respectively) but this was due to the presence of salt in the seawater which reduces the response when comparing with ultra-pure water (see Figure S2). In fact, these two compounds were the ones disadvantaged for the addition of NaCl as we could see in the experimental design optimisation (see Section 3.3). To get good recoveries for this type of water calibration standards containing NaCl (15 %) were prepared. The recoveries obtained were favourable with values of 73 % and 94 % for BPG and BPM, respectively (see Table S3). Mean recoveries are given in Table 3 and, as can be seen they were generally higher than 90 %. The precision in real samples was also suitable for all the samples, and the mean precision values between 6 – 12 % considering all the real samples (seawater, river water, wastewater, and spring water) are also shown.

3.5. Greenness and practicability of the proposed methodology

In recent years, considerable progress has been made in the development of extraction methodologies aligned with the principles of green analytical chemistry (GAC) and green sample preparation (GSP). These strategies aim to utilise safer materials, reagents, and solvents, minimise experimental steps, reduce waste generation and energy consumption, and enhance sample throughput. In 2022, the metric tool AGREEPrep [39] was introduced to assess the environmental sustainability of sample preparation procedures. The sustainability evaluation of the developed SPME-GC-MS method for determining BPs in environmental water samples yielded a favourable greenness profile, with an AGREEPrep score of 0.62. This reflects a well-balanced approach that prioritises sustainability while maintaining high sensitivity and reliability.

The developed method is assessed according to ten criteria, as specified in Fig. 4a: performed in situ, since integration sample preparation and chromatographic analysis is possible using the combiPAL autosampler device (criterion 1); the only hazardous component is

Table 2 ANOVA table for the main factors and two-factors interactions obtained for each BP analogous. Values in bold and italic denote statistical significance (p-value < 0.05).

	A		B		C		D		E		AB		AC	
	Salting-out effect adding NaCl (%)		Acetic Anhydride (µL)		NaHCO ₃ (mg)		Temperature (°C)		Fibre Type		F		P	
	F	P	F	P	F	P	F	P	F	P	F	P	F	P
BPAF	2.34	0.1698	0.34	0.5805	0.22	0.6522	0.55	0.4820	4.35	0.0754	0.08	0.8034	1.02	0.3469
BPF	12.80	0.0090	0.01	0.9357	0.21	0.6596	0.12	0.7429	8.68	0.0215	0.01	0.9193	0.10	0.7608
BPE	14.94	0.0062	0.00	0.9897	0.59	0.4682	0.00	0.9844	8.25	0.0239	0.01	0.9220	0.05	0.8366
BPA	17.03	0.0044	0.00	0.9852	1.30	0.2924	0.48	0.5105	8.14	0.0246	0.07	0.8214	0.15	0.7367
BPG	459.69	0.0022	71.44	0.0137	232.82	0.0043	160.46	0.0062	229.32	0.0043	52.36	0.0186	192.33	0.0052
BPC2	5.21	0.0625	5.69	0.0544	0.01	0.9099	1.97	0.2098	2.94	0.1372	0.19	0.7023	0.13	0.7516
BPC1	1.95	0.2215	0.81	0.4103	2.94	0.1470	5.39	0.0679	5.18	0.0718	1.04	0.3552	1.56	0.2670
BPM	106.95	0.0092	17.48	0.0527	17.93	0.0515	29.62	0.0321	46.74	0.0207	0.45	0.5723	34.83	0.0275
	AD	AE	BC	BD	BE	CD	CE	DE						
	F	P	F	P	F	P	F	P	F	P	F	P	F	P
BPAF	2.97	0.1285	11.21	0.0123	0.57	0.4741	0.02	0.9032	0.00	0.9784	0.94	0.3639	0.00	0.9552
BPF	0.62	0.4561	0.02	0.8942	6.80	0.0350	0.03	0.8797	0.00	0.9533	0.02	0.9017	0.13	0.7255
BPE	0.95	0.3627	3.07	0.1231	7.18	0.0316	0.06	0.8245	0.01	0.9494	0.03	0.8760	0.29	0.6063
BPA	2.16	0.1854	10.09	0.0156	6.30	0.0404	0.13	0.7550	0.00	0.9538	0.03	0.8776	0.56	0.4789
BPG	158.62	0.0062	224.49	0.0044	43.02	0.0225	64.59	0.0151	158.32	0.0063	141.25	0.0070	50.58	0.0192
BPC2	2.53	0.1631	31.69	0.0013	2.51	0.1644	0.56	0.4839	0.02	0.9012	4.16	0.0875	0.13	0.7538
BPC1	2.37	0.1842	26.11	0.0037	1.23	0.3183	0.08	0.8080	0.85	0.3983	0.15	0.7368	0.12	0.7613
BPM	51.62	0.0188	12.19	0.0731	0.17	0.7224	0.12	0.7641	4.15	0.1785	17.63	0.0523	9.22	0.0935
	F	P	F	P	F	P	F	P	F	P	F	P	F	P
BPAF	2.97	0.1285	11.21	0.0123	0.57	0.4741	0.02	0.9032	0.00	0.9784	0.94	0.3639	0.00	0.9552
BPF	0.62	0.4561	0.02	0.8942	6.80	0.0350	0.03	0.8797	0.00	0.9533	0.02	0.9017	0.13	0.7255
BPE	0.95	0.3627	3.07	0.1231	7.18	0.0316	0.06	0.8245	0.01	0.9494	0.03	0.8760	0.29	0.6063
BPA	2.16	0.1854	10.09	0.0156	6.30	0.0404	0.13	0.7550	0.00	0.9538	0.03	0.8776	0.56	0.4789
BPG	158.62	0.0062	224.49	0.0044	43.02	0.0225	64.59	0.0151	158.32	0.0063	141.25	0.0070	50.58	0.0192
BPC2	2.53	0.1631	31.69	0.0013	2.51	0.1644	0.56	0.4839	0.02	0.9012	4.16	0.0875	0.13	0.7538
BPC1	2.37	0.1842	26.11	0.0037	1.23	0.3183	0.08	0.8080	0.85	0.3983	0.15	0.7368	0.12	0.7613
BPM	51.62	0.0188	12.19	0.0731	0.17	0.7224	0.12	0.7641	4.15	0.1785	17.63	0.0523	9.22	0.0935

acetic anhydride, used in minimal volume (50 µL) for analytes derivatisation (criterion 2); a significant contributor to the method sustainability is the extensive reuse of SPME fibres (approx. 200 times), substantially reducing the consumption of consumables and generation of solid waste (criterion 3); the method also produces minimal waste of 15 mL of water sample including 50 µL of acetic anhydride, complying with waste minimisation principles (criterion 4 & 5); throughput is moderate, with two sample prepared per hour, indicating a balance between speed and thoroughness of preparation (criterion 6); the procedure consist of two discrete steps, extraction and thermal desorption, and employs a semi-automated system that minimizes manual intervention while maintaining flexibility (criterion 7); energy consumption is 137.5 Wh per sample due to the power consumption of the stirrer plate (criterion 8); GC–MS is employed as the analytical instrument (criterion 9) and finally, the procedure involves three hazards, including flammable, corrosive and health hazard although, due only to the use of acetic anhydride, but operators safety consideration were carefully addresses (criterion 10).

In addition to the AGREEPrep assessment, the Blue Applicability Grade Index (BAGI), presented in 2023, was also applied to assess practicability [40], yielding a score of 67.5 (Fig. 4b). This score indicates a strong balance between analytical performance and operational feasibility. The BAGI assessment highlights the method’s capability for quantitative and confirmatory (criterion 1); multi-element analysis 9 compounds (criterion 2); using sophisticated instrumentation (GC–MS) (criterion 3); with simultaneous preparation of one sample and miniaturized extraction techniques (criterion 4 & 5); the throughput of 2 samples per hour (criterion 6); and the use of commercially available reagents (criterion 7); further support the method’s applicability in routine laboratory settings. No pre-concentration is required (criterion 8); the semi-automated operation increases efficiency without compromising quality (criterion 9), and finally, water samples (15 mL) can be classified as environmentally friendly (criterion 10).

3.6. Comparison with other methods

Table 4 presents a comparison between the current SPME-GC-MS method and previous analytical methods reported for BPs in various environmental water matrices. The number of BPs analysed in this study (nine compounds) aligns well with or exceeds those in other studies. A major advantage of the present method is the low sample volume required (15 mL), which is considerably less than those employed in the most solid-phase extraction (SPE) methods, where volumes typically vary from 200 to 2000 mL. This reduction in sample volumes improves efficiency and reduces solvent consumption, aligning with green analytical chemistry principles.

The good linearity range (0.005–5 µg L⁻¹) and low LOQ (0.00044–0.0070 µg L⁻¹) achieved by the method demonstrate its high performance which is crucial for detecting BPs at trace levels in environmental waters. LOQs were comparable or superior to earlier methods that reports values between 0.01 ng L⁻¹ and several µg L⁻¹. Recovery rated for most BPs ranged between 91–107 % with RSD ranging from 6 % to 12 %, indicating reliable method accuracy across diverse water matrices such as seawater, river water, wastewater and tap water. These recoveries compare favourably with those previously reported, which typically fall between 70 % and 120 % depending on the analyte and matrix complexity.

An important feature of this study is the application of *in-vial* acetylation derivatisation, which enhances analyte volatility and chromatographic performance while simplifying sample preparation by integrating derivatisation directly in the extraction vial. This approach reduces sample handling time and potential analyte losses and is consistent with green chemistry initiatives, offering advantages over separate derivatisation/extraction steps in other methods. In brief, the proposed SPME method exhibits satisfactory performance and offers several advantages over conventional approaches.

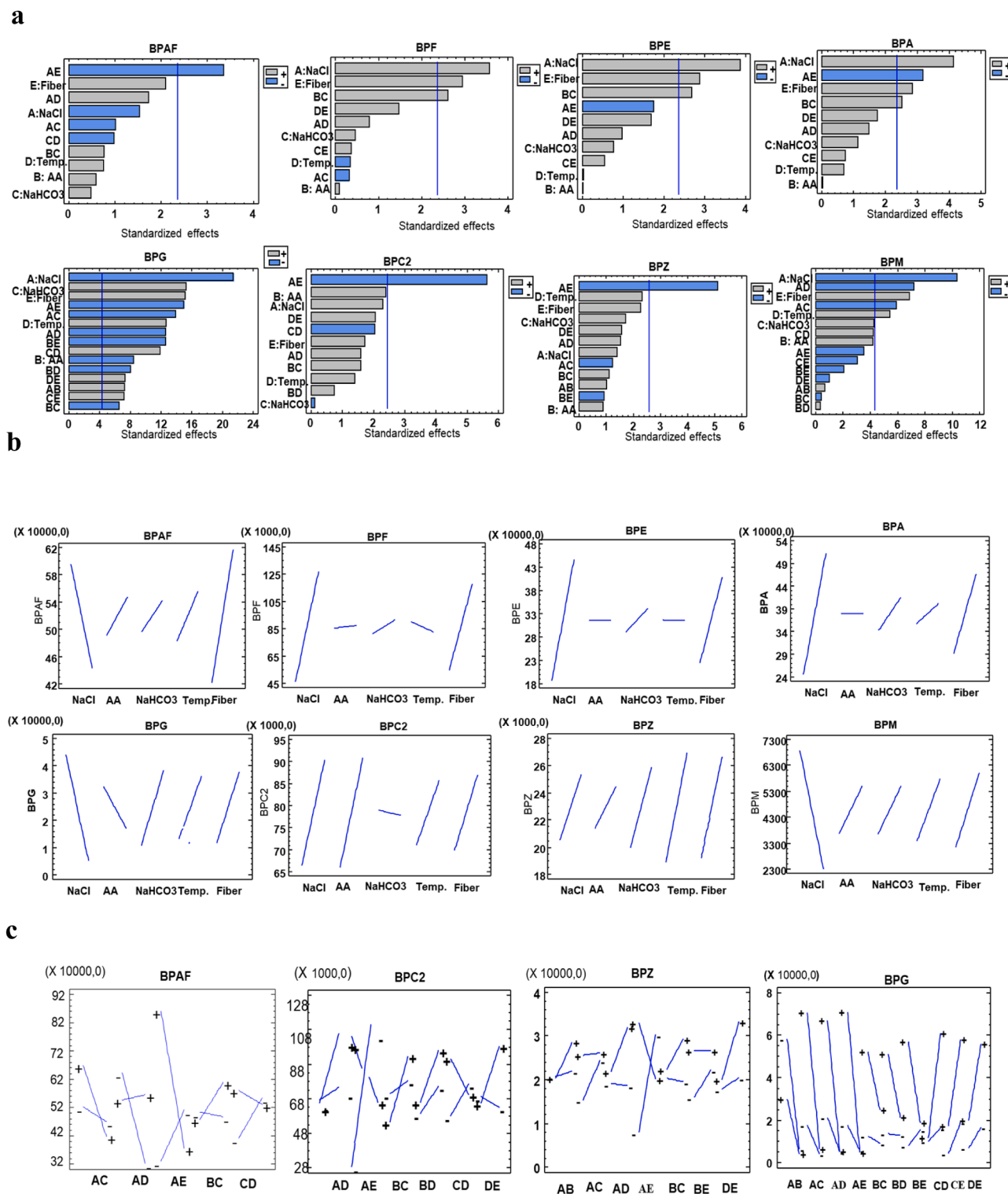


Fig. 2. Experimental design optimisation: a) pareto charts, b) main effects plots, c) interaction plots for the target compounds (see factor codes in Table 1).

3.7. Application to real samples

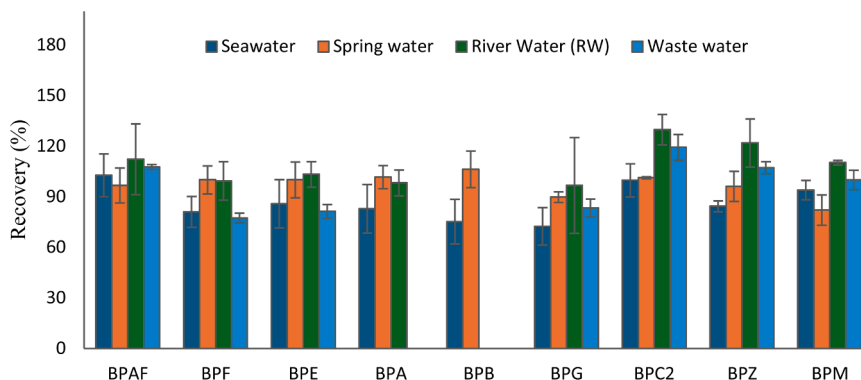
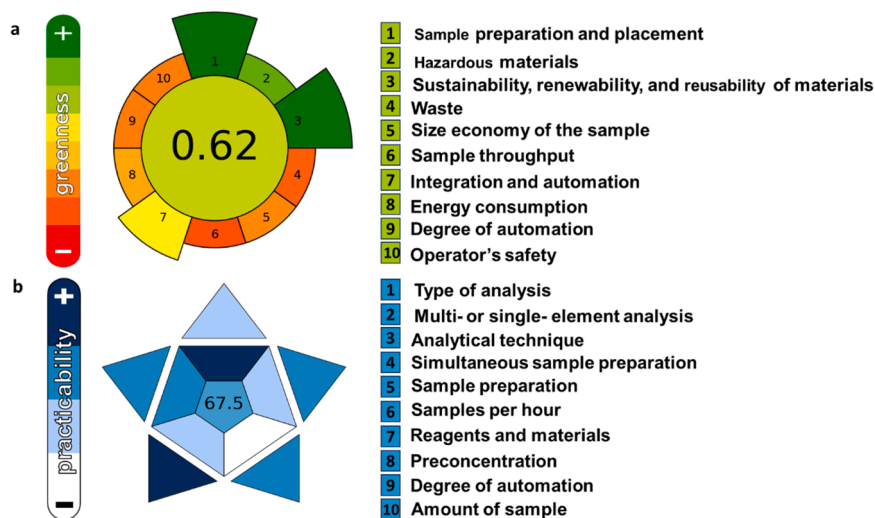
To assess the applicability of the developed SPME-GC-MS method, it was applied to the analysis of real environmental water samples collected from a variety of sources. These included surface waters (rivers and seawater), recreational waters (swimming pools and football field irrigation), drinking water (tap, mineral, and ice cube water), and wastewaters (municipal and port discharges) given a total of 19 samples.

Results are shown in Table 5. Blank cells indicate concentrations below the LOD. Seven out of the nine target BP compounds were found in the analysed samples. BPA was the most frequently detected compound present in 13 of 19 samples, with concentrations ranging from 0.007 to 1.65 $\mu\text{g L}^{-1}$. This prevalence aligns with the previous studies that reported in the referenced review that BPA as a common environmental contaminant due to its extensive industrial use and persistence in aquatic systems [41]. BPF and BPE were detected in eight samples at

Table 3

Linearity, precision, limits of detection and quantification, recoveries and mean precision in real samples.

Compounds	Linearity		Precision (RSD %)		LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Mean recoveries and precision (RSD) in real samples %
	Range ($\mu\text{g L}^{-1}$)	R ²	Intra-day n = 3	Inter-day n = 6			
BPAF	0.005–5	0.9992	16	13	0.00013	0.00044	107 (11)
BPF	0.005–5	0.9995	14	10	0.00088	0.0029	99.7 (9.8)
BPE	0.005–5	0.9993	6.5	20	0.0013	0.0045	93.6 (8.9)
BPA	0.01–5	0.9994	7.9	12	0.0021	0.0070	98.6 (9.0)
BPB	0.005–5	0.999	7.8	12	0.00038	0.0013	90.5 (12)
BPG	0.005–5	0.9992	8.2	13	0.00042	0.0014	86.6 (20)
BPC2	0.005–5	0.9996	8.6	12	0.0004	0.0013	110 (6.7)
BPZ	0.005–5	0.9998	7.2	6.6	0.0013	0.0044	101 (6.4)
BPM	0.02–5	0.9994	9.8	13	0.0043	0.014	97 (7.4)

**Fig. 3.** Recoveries obtained for different water samples: seawater, spring water, river water and wastewater.**Fig. 4.** a) AGREEPrep greenness assessment of the optimised SPME-GC-MS method and, b) BAGI assessment of SPME-GC-MS as practicability of the method for BPs analysis in water matrices.

concentrations between 0.005– 0.038 $\mu\text{g L}^{-1}$ and 0.001–3.48 $\mu\text{g L}^{-1}$ respectively. BPF showed the higher concentration in artificial turf crumb rubber football field irrigation water, while BPE in mineral water collected from the bottom of the water can of drinking water system, possibly reflecting localized contamination sources. BPAF was also found in five samples at concentration from 0.001– 0.006 $\mu\text{g L}^{-1}$, showing the highest concentration in wastewater. BPB was detected in three samples, with concentration up to 0.01 $\mu\text{g L}^{-1}$. BPG and BPC2 were each detected in one sample at concentrations approximately 0.01 $\mu\text{g L}^{-1}$. BPZ and BPM were not detected in any of the samples. Tap water (TW2) and ice cube water (ICW) from the same water source showed comparable results except the higher concentration of BPA in ICW,

which could be due to the leach from the ice cube tray.

Overall, these findings demonstrate the method's high sensitivity and suitability for simultaneous determination of multiple bisphenols in complex environmental water samples. The observed concentration ranges provide valuable insights into the distribution of bisphenol contamination in diverse water sources, underscoring the method's potential for routine analytical use, environmental monitoring and risk assessment programs.

4. Conclusion

An SPME-GC-MS method was developed and validated for the

Table 4

Comparison of the proposed SPME-GC-MS method with other methods developed for the determination of BPs in water samples.

Water matrix	Analytes	Method	Sample volume (mL)	Linearity	LOQ	Recovery (%)	Reference
Tap water, purified water, bottled water	BPA, BPS, BPF, BPAP, BPP, BPAF, BPZ	SPE-LC-MSMS	250	0.01–50 ng mL ⁻¹	0.04–1.0 ng L ⁻¹	77–107	[23]
Coastal and estuarine surface water	BPA, BPF, BPS	SPE-LC-MS/MS	200	0.11–1.56 ng L ⁻¹	5–200 ng L ⁻¹	>90	[24]
River and lake water	BPA, BPAF, BPAP, BPC, BPB, BPF, BPF, BPS, BPZ	SPE-UPLC-MS/MS	500	0.5–200 ng L ⁻¹	0.011–0.077 ng L ⁻¹ (LOD)	80–121 (Milli Q water), 69–114 (spiked samples)	[25]
Wastewater and river water	BPAF, BPAP, BPB, BPC, BPE, BPF, BPS, BPZ	SPE-GCMS (derivatization with MTBSTFA + TBDMCS)	2000	4–100 ng L ⁻¹	0.465–4.13 ng L ⁻¹	Except BPC (56.1)	[12]
Source water and drinking water	BPA, BPAF, BPAP, BPB, BPBP, BPC, BPC2, BPE, BPF, BPG, BPM, BPP, BPPH, BPS, BPTMC, BPZ	SPE-UPLC-MS/MS	500	0.05–50 µg L ⁻¹	0.1–1.7 µg L ⁻¹	73.1–96.9 Except BPPH (57.1)	[13]
Raw (influent) wastewater and treated (effluent) wastewater	BPF, BPE, BPA, BPC, BPB, BPG, BPCl2, BPZ, BPAP	USAEME-GC/MS	5	0.005–500 µg L ⁻¹	correspond to lowest calibration points (0.005 µg L ⁻¹)	88–133 (ultrapure water), 85–119 (raw wastewater), 87–122 (treated wastewater)	[27]
Seawater (Surface and sediment)	BPA, BPAF, BPS, BPF, BPB, DHBP	SPE-UPLC-MS/MS	500	0.1–20 ng mL ⁻¹	0.02–0.36 ng L ⁻¹ (in water), 0.01–0.12 ng g ⁻¹ dw (in sediment)	71–102 (in water), 78–97 (in sediment)	[26]
River and sediment	BPA, BPS, BPF, BPAF, BPAP, BPB, BPC, BPE, DHBP, TDP, TMBPA, TBBPA, TCBPA	LLE-UHPLC-MS/MS (pre-column derivatization)	10	0.005–5.0 ng mL ⁻¹ (water), 0.03–50 ng g ⁻¹ (sediment)	0.005–0.02 ng mL ⁻¹ (water), 0.80 ng g ⁻¹ (sediment)	81.1–119.1 (water), 80.9–111.5 (sediment)	[29]
Seawater, River water, wastewater, spring water, tap water, swimming pool water	BPAF, BPF, BPE, BPA, BPG, BPC2, BPZ, BPM, BPB	SPME-GC/MS (<i>in-vial</i> derivatization with acetic anhydride)	15	0.005–5 µg L ⁻¹	0.0004–0.0069 µg L ⁻¹	89.7–106 µg l ⁻¹ (spring water), 96–8–130 µg l ⁻¹ (river water), 77.4–119 µg l ⁻¹ (wastewater), 72.5–103 µg l ⁻¹ (seawater)	This Study

Table 5Concentration of the target BP compounds in different types of water samples (µg L⁻¹).

	BPAF	BPF	BPE	BPA	BPB	BPG	BPC2	BPZ	BPM
MQ									
SPW1		0.011	0.003	0.084					
SPW 2									
SPW 3	0.001	0.011	3.48	0.021	0.005				
WW1	0.006	0.035	0.006	0.14					
RW				0.007		0.010			
TW1				0.013					
TW2		0.006	0.001						
ICW		0.005	0.003	0.038					
SP1	0.001								
SP2	0.003	0.018	0.001	0.19	0.003				
SW1									
SW2				0.025			0.009		
SW3									
FW1		0.030	0.003	1.65					
FW2	0.003	0.038	0.005	0.40	0.01				
PW1		LOQ		0.32					
PW2				0.23					
PW3				0.43					

MQ: Mili Q water; SPW: Spring water; WW: Wastewater; RW: River water; TW: Tap water; ICW: Ice cube water; SP: Swimming pool; SW: Seawater; FW: Football field irrigation water; PW: Port water; Values in italics are semi quantitative, since they are below the calibration range.

concurrent determination of nine BP compounds in drinking water, wastewater and environmental water samples. A low-cost *in-vial* derivatisation was implemented to enhance the chromatographic response of the BPs. Direct *in-vial* acetylation using inexpensive reagents (NaHCO₃ and acetic anhydride) minimised analyte losses, prevented contamination, and enabled efficient derivatisation within a short timeframe. The key factors effecting the SPME procedure were

optimised through a design of experiments strategy, leading to the identification of optimal operating conditions. The final optimised method employed a DVB/CAR/PDMS fibre under DI extraction conditions at 100 °C for 30 minutes, with the addition of NaCl.

After optimising BP derivatisation with SPME-GC-MS, the method was validated, showing excellent linearity, repeatability, and reproducibility. Recovery experiments across various water matrices

confirmed quantitative recoveries, confirming the accuracy of the method.

Using GC-MS in SIM mode, LODs in the sub- and low $\mu\text{g L}^{-1}$ concentration range were achieved, which is crucial for detecting these emerging pollutants in water samples. Lastly, nineteen real water samples from different origins were analysed and 7 out of the 9 target BPs (BPAF, BPF, BPA, BPB, BPG, and BPC2) were detected. BPA was the most frequently found; it was present in fourteen of the samples.

In summary, the proposed methodology demonstrates both its suitability and high sample throughput for the determination of bisphenols in water samples. Key advantages of the optimised method include its low cost and minimal environmental impact, attributable to the use of only microlitre quantities of organic solvents and the generation of the negligible waste, primarily consisting of the water samples themselves. This methodology thus represents a sustainable approach aligned with the principles of green chemistry.

CRedit authorship contribution statement

Hira Zulfiqar: Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Maria Llompart:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Natalia Montero:** Investigation, Formal analysis, Data curation. **Andres Duque-Villaverde:** Writing – review & editing, Validation, Investigation. **Daniele Fabbri:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.chroma.2025.466453](https://doi.org/10.1016/j.chroma.2025.466453).

Data availability

Data will be made available on request.

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