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Article

A New Approach for Histamine Functionalized Nanoparticles as Sorbent Phase for Bar Adsorptive Microextraction (BAμE) and Determination of Parabens in Water by HPLC-DAD

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In this study, for the first time, histamine-functionalized magnetic nanoparticles (HIS-MNP) were used as sorbent phase combined with bar adsorptive microextraction (BAμE) for the determination of methylparaben (MP), ethylparaben (EP), propylparaben (PP), and butylparaben (BP) in water samples by high performance liquid chromatography coupled with diode array detection (HPLC-DAD). Extraction and desorption conditions, including desorption time and solvent, ionic strength effect and extraction time, were investigated. The extractions were performed for 90 min, 30% of NaCl and sample pH 5. Desorption was carried out using 250 μL of acetonitrile:methanol (25:75 v/v) for 30 min. The limits of detection (LODs) were of 1.5 μg L^{-1} and limits of quantification (LOQs) were 5.0 μg L^{-1} for all analytes. The intra-day precision ranged from 1% for EP, PP and BP to 3% for MP, EP, PP and BP. The inter-day precision ranged from 3% for EP to 18% for BP. The relative recoveries varied from 81 to 125%, and relative standard deviations (RSD) ranged between 1 and 16%.

Keywords: BAμE, liquid chromatography, water sample, parabens, environmental

Introduction

Parabens are esters derived from *p*-hydroxybenzoic acid that are employed as chemical preservatives due to their antimicrobial activity. Therefore, these compounds are widely found in products such as cosmetics, foodstuffs, pharmaceuticals and toiletries. Among the *para*-hydroxy benzoic acid esters, methylparaben, ethylparaben, propylparaben and butylparaben are usually the most used. The antimicrobial activity of these compounds is higher as the alkyl chain increases. However, it ends up limiting the application due to the low solubility in aqueous medium. Recent studies[1-6] have exposed the concern about the damage caused to humans by exposure to these compounds. Some of the problems associated with this exposure are infertility, allergic dermatitis and breast cancer.[4] Based on that, parabens are categorized as endocrine disrupter compounds (EDCs).[2,4-6] These alkyl esters are usually quickly metabolized and excreted in the urine.[1] As a consequence, parabens can be found in environmental compartments, in many cases affecting the quality of water. Hence, the study of these compounds in water is necessary.

Gas chromatography (GC) and liquid chromatography (LC) coupled to some detectors (mass spectrometer (MS) and diode array detector/fluorescence detector (DAD/FLD), respectively) are the most frequently employed techniques to determine parabens. However, due to the low concentration level in which these compounds are found, a sample preparation step is required.[7-10] Solid phase extraction (SPE) and liquid-liquid extraction (LLE) are conventional sample preparation techniques. Although these methods are still much applied for sample preparation, both techniques present many disadvantages, including the use of a large amount of solvents, long preparation times (many hours), laborious and non-environmentally friendly. Thus, microextraction techniques have been widely applied to overcome these limitations. Their advantages are that they are economical, environmentally friendly and simple.[11-14]

Many microextraction techniques have been used to determine parabens in different types of samples, including dispersive liquid-liquid microextraction (DLLME),[9]

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air-assisted liquid-liquid microextraction (AALLME),[15] hollow fiber liquid-phase microextraction (HF-LPME),[16] microextraction by packed sorbent (MEPS),[17] rotating disk sorptive extraction (RDSE),[18] dispersive magnetic micro solid-phase extraction (DμSPE)[19] and bar adsorptive microextraction (BAμE).[20,21]

In the last few years, bar adsorptive microextraction has attracted a lot of attention due to its several advantages, such as speed and ease of preparation and the possibility of choosing the sorbent phase for the extraction of target compounds.[10,22] The BAμE device is composed of a polymeric support coated with the extraction phase with the aid of a double-sided adhesive film. Extraction takes place by flotation technology, wherein the device is less dense than the aqueous sample. Desorption employs only a few microliters of solvent because it involves micro liquid desorption (μLD). One of the main advantages of this technique is the possibility of choosing the most suitable extraction phase based on the compounds to be determined. Many types of sorbent phase have been used in BAμE, among them cork, activated carbon (AC) and carbon nanotubes (CNTs).[10,22-24] The feasibility of using BAμE for extraction of parabens has already been explored by Dias *et al.*[20] and Mafra *et al.*[21] However, in the aforementioned articles cork powder and recycled diatomaceous earth were used to coat the bars. Furthermore, in those works only two selected parabens (methylparaben and ethylparaben) were presented.

Nanoparticles (NPs) used as sorbent phase have been widely applied, owing to properties such as good dispersibility and relatively high surface area. A very interesting feature of NPs is the possibility of functionalization, which allows the NP surface to be modified to increase the selectivity of the method.[25-28] An example is the magnetic nanoparticle functionalized with histamine (HIS-MNP) which was recently proposed by our research group[28] and applied to determine EDCs in aqueous samples by thin-film microextraction (TFME). The TFME/HIS-MNP showed stability, with approximately 40 extraction/desorption cycles and limits of detection (LOD) and quantification (LOQ) comparable with other related works in literature.

This work presents a new approach for the use of nanoparticles functionalized with histamine along with BAμE. The method was used for the determination of parabens in aqueous samples by high performance liquid chromatography coupled with diode array detection (HPLC-DAD). The approach proved to be promising and can be used to analyze other types of samples and other classes of compounds.

Experimental

Instrumentation

The HPLC-DAD analysis was carried out on a Shimadzu Prominence LC 20AT series HPLC system (Shimadzu, Kyoto, Japan) equipped with a diode array detector (SPD-M20 A series), a loop of 20 μL and a Rheodyne 7725i manual injector (Rohnert Park, CA, USA). The chromatographic separation was performed in a C18 column (Agilent, 250 × 4.6 mm i.d., 5 μm film thickness). The gradient elution mode was selected and the mobile phase consisted of a mixture of water (A) 55%, and acetonitrile (ACN, B) 45% at 0-2.5 min, followed by: 2.5-4.0 min increase B to 80% and kept constant up to 7.5 min; mobile phase B was then decreased to 45% at 7.5-10.0 min. The flow rate of the mobile phase was 1.0 mL min^{-1} and the detector was set at 254 nm as maximum wavelength for determination of the parabens. The chromatographic data were evaluated using LC Solution software (Shimadzu, Kyoto, Japan).

For the characterization of the nanoparticles, the infrared spectrophotometer PerkinElmer Spectrum 100 (PerkinElmer, Massachusetts, USA) was used in the region of 4000 to 500 cm^{-1}. Solid samples were analyzed using attenuated total reflectance (ATR). Analyses were performed at each synthesis step, to make sure that the material was correct and to proceed with the next functionalization step. Thermogravimetric analysis was carried out on a Thermogravimetric Analyzer model TGA-50 (Shimadzu, Kyoto, Japan). Samples were heated to 800 °C at 10 °C min^{-1} under the N_2 atmosphere. Transmission electron microscopy (TEM) was conducted using a JEOL JEM-1011 (Peabody, USA) instrument operating at 100 kV.

Reagents and materials

The parabens methylparaben (MP), ethylparaben (EP), propylparaben (PP), and butylparaben (BP) were purchased from Sigma-Aldrich (St. Louis, MO, USA) all of high-purity analytical grade (99%). Acetonitrile (ACN) and methanol (MeOH), both HPLC grade, were purchased from JT Baker (Mallinckrodt, NJ, USA). Ultrapure water was purified by the Mega Purity water purification system (Billerica, MA, USA). Stock solutions containing 1000 mg L^{-1} of each analyte were prepared in MeOH. Working solutions containing each analyte (50 mg L^{-1}) were prepared by diluting the stock solutions in MeOH. Citric acid and disodium hydrogen phosphate used to prepare the buffer solutions were obtained from

Vetec (Rio de Janeiro, Brazil). Sodium chloride used for the evaluation of the salting out effect was also purchased from Vetec (Rio de Janeiro, Brazil). Magnetic stirrers (Fisatom, São Paulo, Brazil) were employed for agitation of samples through a Variac Tension Regulator TDGC2-1 1KVA/4AMP (EZA Instruments, São Paulo, Brazil) by a power strip (NBR 20605, Power Line) and a Digital Multimeter ET-1002 (Minipa, São Paulo, Brazil) used to control the voltage.

Preparation of magnetic nanoparticles (MNPs)

Based on the literature,[29] the OA-MNP (nanoparticles stabilized with oleic acid) were synthesized. In 100 mL of deionized water were dissolved 10 mmol of $FeCl_3$ and 5 mmol of $FeCl_2.4H_2O$, using a three-neck round-bottom flask, and mechanically agitated at 80 °C, employing argon bubbling. After 30 min, the amount of 10 mmol of potassium oleate was added and the solution was stirred for another 30 min. Thereupon, 35 mL of NH_4OH_{aq} (4%) was rapidly added and a black dispersion was instantly formed. The synthesis proceeded for 30 min at 80 °C, and the monodispersed OA-MNP at 54 mg mL^{-1} present in the black dispersion was stored under argon atmosphere.[28]

The copolymerization of glycidyl methacrylate (GMA) with OA-MNP was carried out in a Schlenck flask. In 100 mL of the aqueous dispersion of OA-MNP were added 4.6 mL of GMA and 360 mg of ammonium persulfate (APS). Argon was used to purge the mixture, and the flask was placed in a preheated silicon bath at 80 °C. Under argon flow and magnetic agitation, the synthesis proceeded for 1 h. After cooling, with the aid of a strong magnet, the GMA-MNP (magnetic nanoparticles coated with glycidyl methacrylate) were collected, and large amounts of water and ethanol were used for rinsing (approximately 10 times).[28]

The functionalization of the GMA-MNP was carried out via epoxy ring opening with histamine. In 10 mL of an aqueous solution containing 20 mmol histamine, the amount of 1 g of GMA-MNP was dispersed and, at room temperature, the mixture was magnetically agitated for 3 days. Lastly, with the aid of a strong magnet, the MNP@OA-GMA-HIS particles were collected and washed many times with water and ethanol (approximately 10 times).[28]

Preparation of the HIS-MNP adsorptive bars

The preparation of the bars was conducted according to previous publications of our group.[20,21] Polypropylene hollow cylindrical tubes (7.5 mm length and 3 mm diameter) were covered with double-sided tape (Adelbras, Ind. e Com. de Adesivos, 6 mm height × 10 mm width) that was employed to fix the sorbent (HIS-MNP) in the bars. The conditioning of the bars occurred using 250 µL (using vials with capacity of 300 µL) of acetonitrile for 30 min, after which 300 µL of ultrapure water was used for another 30 min. This procedure was applied until the unadhered particles of the extraction phase was removed and orbital stirring was used in both stages. The amount of material was limited to the size of the bar, with the double-sided tape material homogeneously covered at the finale.

Optimization steps

Some extraction and desorption parameters were assessed to improve the extraction efficiency, as follows below:

Desorption conditions

(*i*) Desorption time: the desorption time was studied using a univariate design that varied from 10 to 30 min; (*ii*) type of desorption solvent: ACN, MeOH and water were evaluated as desorption solvent, employing a simplex-lattice design. The volume of 250 µL was selected because it was the smallest that covered the entire bar.

Extraction conditions

Extraction time and salt concentration were analyzed through a Doehlert design. The extraction time ranged from 30 to 90 min, and percentage of NaCl ranged from 0 to 30%. The pH was not investigated because the analytes are non-ionizable in the studied sample; thus pH 5 was fixed for the optimization (mean value between the ultrapure water used in methodology development and the samples).

Optimized extraction procedure using BAµE

The extractions were carried out in vials with capacity of 22 mL with 15 mL of ultrapure water spiked with 500 µg L^{-1} of the parabens (this sample volume is ideal to guarantee the vortex to extraction process). In addition, the sample pH was maintained to 5, NaCl at 30% and the extraction time 90 min. With the aid of a stainless-steel wire in the shape of a handle, the floating bar was inserted in the water sample. Magnetic stirring was used throughout the process. The desorption step was performed with 250 µL (vials with capacity of 300 µL) of ACN:MeOH (25:75 v/v) for 30 min, and orbital stirring was employed in all assays.

After extraction and desorption, the bars were cleaned in ACN for 30 min and then in ultrapure water for an

additional 30 min. In this study, six extractions were performed simultaneously, employing six magnetic stirrers connected to a Variac Tension Regulator by a power strip, and the voltage was controlled by a Digital Multimeter at 145 ± 1 V.

Water samples

The water samples were collected near a Federal University of Santa Catarina (UFSC), following: (*i*) lake water of the premises of University Hospital (HU), coordinates: 27°36'07.6"S 48°31'15.2"W; (*ii*) stream water from the University Stream (CU), coordinates: 27°35'53.1"S 48°31'22.6"W; (*iii*) swamp water located around the University, coordinates: 27°35'33.9"S 48°30'52.0"W.

After collection, the samples were stored at 4 °C in amber flasks until analysis. The samples were filtered prior analysis using a polytetrafluoroethylene (PTFE) filters with 0.45 µm of pore size obtained from Allcrom (São Paulo, Brazil).

Results and Discussion

Characterization of the nanoparticles (MNPs)

The characterization of HIS-MNP has been previously conducted by Lopes *et al.*[28] (Figures S1 and S2, Supplementary Information (SI) section). To confirm the presence of the polymeric group GMA in the OA-MNP, transmission electron microscopy (TEM) was conducted (Figure S1), which exhibited an increase in the particle size. Both are spherical particles, but while the OA-MNP has a diameter of 9 nm, the GMA-MNP has a diameter around 400 nm. Thus, this difference shows the insertion of the GMA polymer. A thermogravimetry (TGA) analysis demonstrated approximately 93% of organic material in the GMA-MNP.[28]

In the work of Lopes *et al.*,[28] the nanoparticles were also analyzed by Fourier transform infrared spectroscopy (FTIR) wherein OA-MNP presented C–H alkyl stretch (2850-2950 cm^{-1}), bands of carboxylate group (1523 and 1420 cm^{-1}) and Fe–O bonds (600 cm^{-1}). The band of ester carbonyl stretch (1722 cm^{-1}), bands of epoxy ring bending (905 and 842 cm^{-1}) and the non-appearance of C=C band (ca. 1640 cm^{-1}) evidence the insertion of the GMA group (Figure S2). Absence of epoxy ring signals, band of N–H deformation (1565 cm^{-1}) and bands of N–H and O–H stretches (3600-3200 cm^{-1}) characterize the insertion of the histamine group. Scanning electron microscopy (SEM) and elemental analysis demonstrated that the material studied is porous and homogeneous, and the amount of histamine in the material is 1.46 mmol g^{-1}.[28]

Chromatographic separation and optimizations

The analytes were separated using the mobile phase demonstrated in Instrumentation sub-section, using ACN and ultrapure water in the HPLC-DAD system, obtaining a chromatographic run of 10 min with the established wavelength of 254 nm. Figure S3 (SI section) shows the separation between the analytes, being an extraction of 50 µg L^{-1} in ultrapure water with retention times for MP in 3.4 min, EP in 4.1 min, PP in 5.4 min and BP in 7.3 min.

Optimization steps

First, desorption was made to ensure that the analytes were desorbed and to obtain peaks in the chromatographic system. This is an important step in sample preparation and, to obtain the maximum analytical response, desorption time and type of desorption solvent were studied. Desorption time was evaluated in a univariate mode for 10, 20 and 30 min of desorption and the results are presented in Figure 1. According to Figure 1, the optimum condition was obtained when 30 min was used. It is noticed that with 30 min there is already a stabilization in the normalized peak area. When 10 min was used, the lowest desorption efficiency was obtained. A possible explanation is that this was not enough time for a good interaction between the solvent and the compounds. For the desorption time of 20 min, the responses were very close to those of 30 min. However, this time presented higher relative standard deviation (RSD), and to guarantee the maximum desorption of the analytes 30 min was chosen.

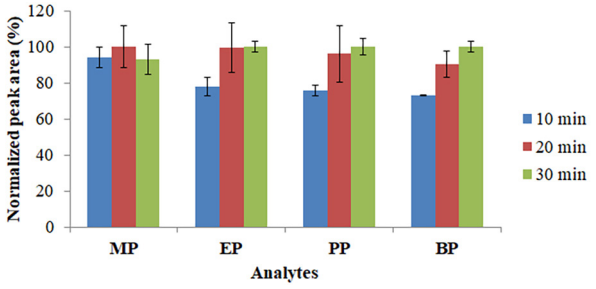

Figure 1. Optimization of desorption time using 250 µL of ACN as the desorption solvent. Experimental conditions: 15 mL of ultrapure water sample spiked with 500 µg L^{-1} of parabens, sample pH 5.0, no salt addition and extraction time of 60 min. Analytes: methylparaben (MP), ethylparaben (EP), propylparaben (PP) and butylparaben (BP).

For selecting the type of desorption, solvent ACN, MeOH and ultrapure water were evaluated using a

simplex-lattice design and geometric mean of the peak areas as response (Figure 2). According to Figure 2, ultrapure water did not prove to be viable, as it does not have a good interaction to remove the analytes from the phase. The mixture of ACN and MeOH showed better results. From the use of 50% MeOH there was an increase in the analytical response. The trend indicates responses closer to methanol, however, with the mixture of ACN in small proportion it was possible to obtain a better response, because the analyte and extracting phase interaction was overcome, thus, a combination of 25% ACN and 75% MeOH was chosen.

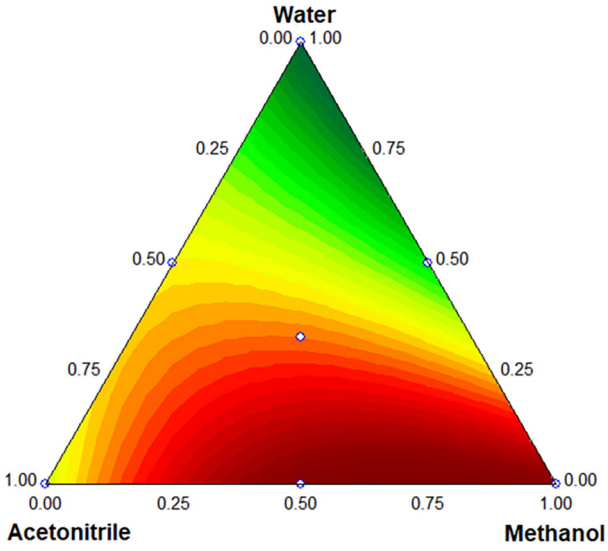

Figure 2. Optimization of desorption solvent using 30 min as desorption time. Experimental conditions: 15 mL of ultrapure water sample spiked with 500 μg L^{-1} of parabens, sample pH 5.0, no salt addition and extraction time of 60 min. Analytes: methylparaben (MP), ethylparaben (EP), propylparaben (PP) and butylparaben (BP).

The BAμE is not an exhaustive extraction technique so it is necessary to achieve the equilibrium condition for a quantitative extraction of the target analytes. Thus, extraction time is an important variable to study since it is dependent on the kinetics of mass transfer of the compounds in the sorbent phase and in the aqueous phase.[30-33] The salt concentration can also influence the extraction efficiency due to salting out effect. That occurs when the solvated water prefers the salt ions, decreasing the solubility of the analytes in the sample and favoring their migration to the sorbent phase.[31,33] Then, NaCl concentration (0-30%) and extraction time (30-90 min) were optimized, employing a Doehlert design using geometric means of the peak areas of the analytes as response (Figure 3).

According to Figure 3, the longer the extraction time the greater the response obtained. The same behavior was observed for the salt concentration, since extraction

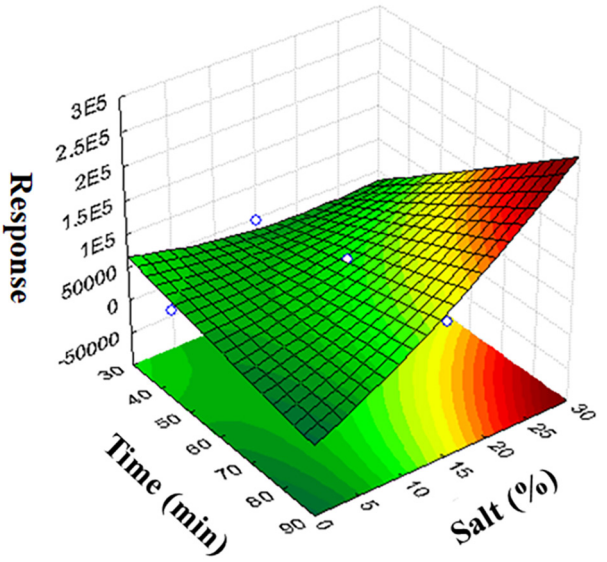

Figure 3. Response surface obtained using a Doehlert design for the optimization of extraction time and NaCl concentration. Experimental conditions: 15 mL of ultrapure water sample spiked with 500 μg L^{-1} of parabens, sample pH 5.0, desorption time of 30 min in ACN:MeOH (25:75) (v/v). Analytes: methylparaben (MP), ethylparaben (EP), propylparaben (PP) and butylparaben (BP).

efficiency increased when using the maximum salt percentage. Thus, the extraction time of 90 min and 30% of NaCl were selected. Considering extraction and desorption steps, the total sample preparation time was 120 min.

Analytical parameters of merit and analysis of samples

For each compound, a calibration curve (7 standard points) was constructed applying optimized extraction and desorption conditions in water samples, and the analytical parameters of merit were obtained. Determination coefficients (r^2), linear working range, LOD, LOQ and precision (RSD) were determined. The data are exhibited in Table 1. For all analytes, the r^2 was greater than 0.99 and the linear working range varied from 5 to 500 μg L^{-1}. The LOQ was stablished as the first point on the curve due to being the smallest quantifiable point by the method, with LOD calculated as LOQ divided by 3.3. LODs and LOQs were of 1.5 and 5.0 μg L^{-1}, respectively, for all compounds. The intra-day precision ranged from 1% for EP, PP and BP to 3% for MP, EP, PP and BP, and inter-day precision ranged from 3% for EP to 18% for BP.

Relative recoveries of the analytes in samples of lake, stream and swamp water were used for assessing the accuracy of the method. The water samples were spiked at concentrations of 5, 50 and 500 μg L^{-1} of the analytes in replicates (n = 3). Results are shown in Table 2. According to Table 2, the relative recoveries varied from

Table 1. Linear range, determination coefficients (r^2), limits of detection (LOD), quantification (LOQ) and precision obtained for proposed method for extraction of parabens in urine samples using HIS-MNP/BAμE

Analyte	Linear working range / (μg L^{-1})	LOD / (μg L^{-1})	LOQ / (μg L^{-1})	r^2	Precision (intraday)[a] (n = 3)		Precision (interday)[a] (n = 9)	
					μg L^{-1}	%	μg L^{-1}	%
MP	5.0-500.0	1.5	5.0	0.9971	5.0	3	5.0	11
					50.0	2	50.0	12
					500.0	2	500.0	10
EP	5.0-500.0	1.5	5.0	0.9963	5.0	1	5.0	3
					50.0	1	50.0	12
					500.0	3	500.0	12
PP	5.0-500.0	1.5	5.0	0.9961	5.0	1	5.0	12
					50.0	1	50.0	9
					500.0	3	500.0	10
BP	5.0-500.0	1.5	5.0	0.9961	5.0	3	5.0	18
					50.0	3	50.0	5
					500.0	1	500.0	8

[a]Intra-day and inter-day precisions were calculated based on relative standard deviation (RSD).

81 to 125%, and relative standard deviations (RSD) varied from 1 to 16%. In the analysis of non-spiked samples, the concentrations of the parabens were below the LOD of the proposed method.

A comparison of the proposed method with other works previously reported in the literature is presented in Table 3. The LODs obtained were lower[2,20,34,35] or similar[36] being only higher than Almeida and Nogueira,[37] thus providing a satisfactory result, and the linear working ranges were also comparable, ranging from 5 to 500 μg L^{-1}. The extraction time of 90 min is similar to some other works.[20,36] However, it is possible to perform more than one extraction at the same time, which is advantageous when thinking about high throughput analysis. The method also evaluates the 4 parabens simultaneously, different from the other works[2,20,35] which reported the extraction of two or three parabens. In addition, the HIS-MNP presented a high surface area and good porosity, collaborating with the method's selectivity. The proposal to use BAμE with this nanomaterial is an unprecedent methodology, and was proved to be a successful and promising method in this application.

Reproducibility and stability of the HIS-MNP as an extraction phase for BAμE

The reproducibility of the HIS-MNP combined with BAμE was verified using six different bars for simultaneous extractions and 500 μg L^{-1} for the analytes. The RSD between the bars varied from 5% for methylparaben to 13% for butylparaben. These results are shown in Table S1 (SI section). All RSDs were less than 20% and the proposed technique was considered reproducible. In addition, the stability of the HIS-MNP presented in Figure S4 (SI

Table 2. Relative recovery and precision expressed as relative standard deviation using the proposed method (n = 3)

Analyte	Spiked level / (μg L^{-1})	Lake water sample		Stream water sample		Swamp water sample	
		Rec. / %	RSD / %	Rec. / %	RSD / %	Rec. / %	RSD / %
MP	5.0	89	10	84	1	93	3
	50.0	119	5	100	6	104	8
	500.00	125	2	111	1	118	2
EP	5.0	99	4	117	2	114	6
	50.0	110	9	97	6	93	1
	500.00	116	8	96	4	111	16
PP	5.0	95	6	101	3	95	8
	50.0	84	1	82	7	81	9
	500.00	111	8	96	6	111	3
BP	5.0	89	3	82	4	105	9
	50.0	94	2	99	7	99	1
	500.00	103	8	90	9	102	4

Rec.: relative recovery; RSD: relative standard deviation. MP: methylparaben; EP: ethylparaben; PP: propylparaben; BP: butylparaben.

Table 3. Comparison of the proposed method with studies previously reported in the literature

Reference	Analyte	LOD / (μg L^{-1})	Linear range / (μg L^{-1})	Extraction technique	Extraction time	Analytical technique
This study	MP	1.5	5.0-500.0	HIS-MNP/BAμE	90 min	HPLC-DAD
	EP	1.5	5.0-500.0			
	PP	1.5	5.0-500.0			
	BP	1.5	5.0-500.0			
34	MP	2.2	5.0-1000.0	SPE-LVSS	60 s	CE–DAD
	EP	2.3	5.0-1000.0			
	PP	1.9	5.0-1000.0			
	BP	1.8	5.0-1000.0			
20	MP	2.5	8.0-400.0	Cork/BAμE	90 min	HPLC-DAD
	EP	1.0	3.2-400.0			
35	EP	3.5	–	DF-μLPME	5 min	HPLC-DAD
	PP	1.8	–			
	BP	2.6	–			
36	MP	1.5	5.0-500.0	Pa-SDME	90 min	HPLC-DAD
	EP	1.5	5.0-500.0			
	PP	1.5	5.0-500.0			
	BP	1.5	5.0-500.0			
2	MP	3.5	10.0-1000.0	MSPE-MNP@ DC193C	10 min	HPLC-UV
	EP	5.0	10.0-1000.0			
	PP	6.3	10.0-1000.0			
37	MP	0.1	0.5-28.0	BAμE	16 h	HPLC-DAD
	EP	0.1	0.5-28.0			
	PP	0.1	0.5-28.0			
	BP	0.1	0.5-28.0			

LOD: limit of detection; MP: methylparaben; EP: ethylparaben; PP: propylparaben; BP: butylparaben; HIS-MNP/BAμE: histamine-functionalized magnetic nanoparticles/bar adsorptive microextraction; HPLC-DAD: high performance liquid chromatography coupled with diode array detection; SPE-LVSS: solid phase extraction-large volume sample stacking; CE-DAD: capillary electrophoresis- diode array detection; Cork/BAμE: cork/bar adsorptive microextraction; DF-μLPME: double-flow microfluidic-based liquid-phase microextraction; Pa-SDME: parallel single-drop microextraction; MSPE-MNP@DC193C: magnetic solid phase extraction-nanoparticles@surfactant DC193C; BAμE: bar adsorptive microextraction.

section) was found as eighteen extraction/desorption cycles presenting up to 80% of efficiency. All the RSDs obtained are below 7.5% for the 4 analytes in 500 μg L^{-1}, thus, extractions and desorption can be performed 18 times using the same bar and without carryover.

Conclusions

HIS-MNP used as sorbent for BAμE was successfully applied to the determination of MP, EP, PP and BP in water samples. The developed approach displayed satisfactory results, including those for LODs, LOQs, determination coefficients, relative recovery and precisions. The method is environmentally friendly and does not require any additional solvent. In addition, HIS-MNP/BAμE is low-cost and can be reused for 18 extraction/desorption cycles without losing significant efficiency. As well as its ease of application, the procedure can be used for analysis of other samples and various types of compounds. Moreover, HIS-MNP provided good extraction of the target analytes and assays free of carryover.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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Author Contributions

Eduardo Carasek was responsible for the conceptualization, writing review and editing, project administration, funding acquisition and supervision; Daniela Lopes for the methodology, validation, formal analysis, investigation, writing original draft; Lucas Morés

for the methodology and investigation; Roberta Campedelli for the methodology and investigation; Gabrieli Bernardi for the conceptualization, writing review and editing; Gabriela Pinheiro for the methodology and investigation; Bruno S. de Souza for the conceptualization, writing review and editing.

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