



Determination of parabens in waters by magnetically confined hydrophobic nanoparticle microextraction coupled to gas chromatography/mass spectrometry



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ABSTRACT

In this article, magnetically confined hydrophobic nanoparticle microextraction is applied for the analysis of parabens in water samples by gas chromatography (GC)–mass spectrometry (MS). The hydrophobic magnetic nanoparticles (MNPs) are confined in a device by means of a mini-magnet which also allows the stirring of the unit. A thin layer of MNPs, which presents an optimal surface to volume ratio, is the responsible of the analytes extraction. Although the superficial area of the layer is lower than the potential one obtained with a perfect dispersion of the MNPs, the latter approach is hard to be performed with highly hydrophobic MNPs and therefore the proposed configuration is more useful from a practical point of view. This fact, together with the inherent stirring of the unit, enhances the kinetic extraction and therefore the sensitivity of the procedure compared to conventional dispersion conditions. The most influential extraction parameters were evaluated, including the pH and ionic strength of the sample, the stirring rate, the extraction time, the amounts of MNPs, the volume of sample and the elution conditions. Under the most favorable extraction parameters, the method showed good linearity, repeatability (relative standard deviation below 7.1%, $n = 7$) and sensitivity in the ng per liter range. The proposed method was demonstrated to be a simple, fast and efficient method for the analysis of parabens in sea and swimming pool water samples.

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1. Introduction

Parabens are a group of alkyl esters of the p-hydroxybenzoic acid that are widely used as preservatives in pharmaceutical and personal care products (e.g.; solar lotions, deodorants, hair gels, shampoos, creams and toothpastes) due to their broad anti-microbial spectrum and effectiveness. Their anti-microbial activity increases with the length of the alkyl side chain from methyl to butyl. Parabens have multiple biological actions, but it is generally described that their inhibitory effects on membrane transport and mitochondrial function processes are keys for their actions [1]. Since their potential contribution to the incidence of breast cancer has been highlighted [2–6], the use of these preservatives in cosmetics has been discussed worldwide.

As personal care products, parabens are continuously released into the environment through urban wastewater. Although they are relatively polar compounds that can be effectively removed during conventional sewage treatment [7–11], they have already been detected in surface waters at the ng/L level [9,10,12–14]. Moreover as parabens are usual components in sunscreen formulations, they can be present in sea water and swimming pool water. On the one hand, their occurrence in sea water is a problem of environmental concern

since some parabens (especially butylparaben) can cause complete coral bleaching even at very low concentrations [15]. On the other hand, parabens can be found in swimming pool water as parent compounds and chlorinated by-products [16]. Thus, simple and sensitive analytical methods are required in order to understand the fate and distribution of this kind of emerging contaminants in the environment.

The determination of parabens in water samples is usually accomplished by gas chromatography (GC) or liquid chromatography (LC). Due to the low concentration of the analytes in real samples, a previous preconcentration step is required. Solid phase extraction (SPE) is the common alternative of choice [9,10,17–22] since it allows for processing high sample volumes in a simple procedure. However, solid phase microextraction (SPME) has been firmly established as a valuable alternative to SPE methods [7,8] in the last years thanks to its low sample requirement to accomplish similar enrichment factors. Moreover, SPME requires a lower amount of organic solvents to be developed and it is easily coupled, even integrated, with commercial analytical instrumentation. In addition to SPE and SPME approaches, new microextraction techniques such as single-drop-microextraction (SDME) [23], ultrasound-assisted emulsification–microextraction [11] or membrane-assisted liquid–liquid extraction [24] have been proposed to extract parabens from water samples.

Recently a new extraction approach, called magnetically confined hydrophobic nanoparticle microextraction [25], has been proposed to

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take advantage of the special properties of octadecyl functionalized magnetic nanoparticles. This technique limits the aggregation tendency of these hydrophobic magnetic nanoparticles (MNPs) which can be considered their main drawback. The hydrophobic NPs are deposited in a special extraction device by means of a mini-magnet, which also allows the sample stirring in order to enhance the transference of the target analytes from the bulk sample to the extracting phase. The technique was evaluated for the determination of bisphenol A, 4-tert-butylphenol, 4-cumylphenol, 4-tert-octylphenol, 4-nonylphenol and 4-octylphenol in water by LC.

In this article, a new method for the extraction and determination of parabens in water samples is presented. The analytical procedure is based on a derivatization of the analytes with acetic anhydride, being the derivatized compounds finally isolated/preconcentrated by magnetically confined hydrophobic nanoparticle microextraction. The proposed method has been successfully applied to the determination of parabens in sea water and swimming pool water.

2. Experimental

2.1. Reagents, materials and samples

All reagents were of analytical grade or better. Sigma-Aldrich (Madrid, Spain) provided the analytes: methyl 4-hydroxybenzoate (methyl-paraben), ethyl 4-hydroxybenzoate (ethyl-paraben), propyl 4-hydroxybenzoate (propyl-paraben) and butyl 4-hydroxybenzoate (butyl-paraben). Stock standard solutions of each analyte were prepared in methanol (Scharlab, Barcelona, Spain) at a concentration of 1 g/L and stored in the dark at 4 °C. Working solutions were prepared by a rigorous dilution of stock solutions with methanol or Milli-Q ultrapure water (Millipore Corp., Madrid, Spain) as required.

Acetic anhydride and potassium carbonate, which were used for the analyte derivatization, were also purchased from Sigma-Aldrich. All the reagents required for the synthesis of the magnetic nanoparticles were also obtained from Sigma-Aldrich. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and ammonia were used for the synthesis of the magnetic core (Fe_3O_4). Tetraethyl orthosilicate (TEOS) and ethanol were employed for covering the magnetic core with a protective silica-based coating. Finally, octadecyltriethoxysilane and toluene were used to introduce hydrophobic groups on the nanoparticle surface.

Water samples, sea water (from the south coast of the Spain, collected near the shore) and swimming pool water, were collected in amber-glass bottles without headspace. The samples were stored in the dark at 4 °C until their analysis.

2.2. Apparatus

Gas chromatographic/mass spectrometric analyses were carried out on an HP6890 gas chromatograph equipped with an HP5973 (Agilent) mass spectrometric detector based on a quadrupole analyzer and an electron multiplier detector. System control and data acquisition was achieved with an HP1701CA MS ChemStation software (Agilent Technologies, Palo Alto, CA). Chromatographic separations were performed on a fused silica capillary column (30 m \times 0.25 mm i.d.) coated with 5% diphenylsiloxane and 95% dimethylsiloxane (film thickness 0.25 μm) (Supelco, Madrid, Spain). The column temperature program was as follows: 1 min at 60 °C, raised up to 150 °C at 25 °C min^{-1} , then immediately ramped at 3 °C min^{-1} up to 170 °C and raised up to 280 °C at 25 °C min^{-1} and kept finally at this temperature for 2 min. A column split ratio of 1:10 was selected for injection. Helium (6.0 grade purity, Air Liquide, Seville, Spain), at a flow rate of 1 mL/min, regulated by a digital pressure and flow controller, was used as carrier gas.

Electron impact ionization (70 eV) was used for analyte fragmentation. The quadrupole mass spectrometer detector was operated in selected ion monitoring mode, recording 121 and 138 m/z ions. The

MS source and quadrupole temperatures were maintained at 230 and 150 °C, respectively. The peak areas were used for quantification of individual analytes.

2.3. Synthesis and characterization of magnetic nanoparticles

MNPs are prepared as described in our previous work [25] following three main steps. First, the magnetic core (Fe_3O_4) was obtained by coprecipitation. For this aim, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (24 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (9.8 g) were dissolved in 100 mL of water under nitrogen atmosphere, vigorously stirred and maintained at 80 °C in a water bath for 30 min. Then, 50 mL of ammonia (25 wt.%) were added dropwise producing a black precipitate of Fe_3O_4 . The MNPs were separated with an external magnet, washed with water to remove the unreacted chemicals, and finally dried.

In a second step, the MNPs were covered with a silica coating in order to protect the magnetite core. The $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles were obtained by dispersing Fe_3O_4 nanoparticles in ethanol/water (50 mL/4 mL) solution in the presence of TEOS (2 mL) under a nitrogen atmosphere. The dispersion was stirred overnight and the protected magnetic nanoparticles were recovered with an external magnet, thoroughly washed with water and dried.

Finally, the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles were dispersed in 50 mL of anhydrous toluene containing 1% (v/v) of octadecyltriethoxysilane. The mixture was sonicated for 5 min and refluxed for 12 h. The obtained nanoparticles ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{C}_{18}$) were washed several times with ethanol and dried, yielding a fine powder of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{C}_{18}$.

The synthesized nanoparticles were characterized by FT-IR spectroscopy and microscopy. The particle size and structure of MNPs were observed by using a transmission electron microscopy (TEM). They show a spherical morphology and an average particle size of 10 nm. The IR spectrum obtained under the attenuated total reflection sampling mode shows a characteristic band of Fe_3O_4 around 600 cm^{-1} which corresponds to the Fe–O bonds and a strong absorbing region at 1200–1000 cm^{-1} characteristic of the Si–O–H and Si–O–Si bonds. Moreover, the characteristics C–H stretching vibrating bands of octadecyl groups of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{C}_{18}$ MNPs can be observed at 2920 and 2850 cm^{-1} .

2.4. Magnetically confined MNPs unit design

The extraction unit is described elsewhere [25] and it consists of four commercial elements, namely: (a) a cube-shaped magnet (5 mm in length and 10.8 N of maximum adhesive force) purchased from Supermagnete (Gottmadingen, Germany), (b) a PTFE septum (c) a PTFE top-cap commercially available for the SPE cartridges, and (d) an

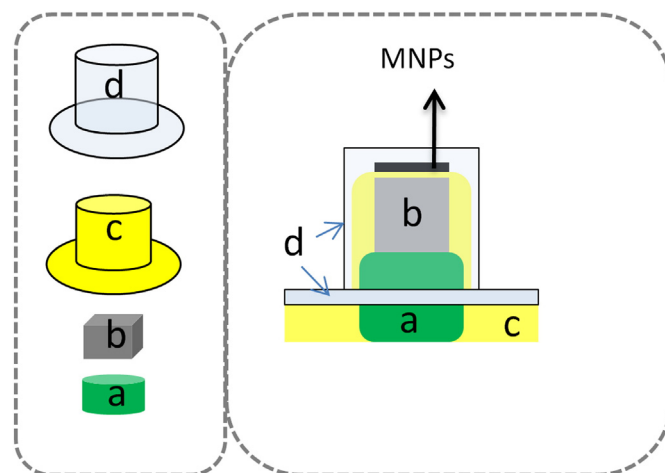


Fig. 1. Schematic view of the extraction device.

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