Journal of Chromatography A, 1564 (2018) 102–109

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Magnetic carbon nanotube composite for the preconcentration of parabens from water and urine samples using dispersive solid phase extraction☆

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ARTICLE INFO

Article history:
Received 26 April 2018
Received in revised form 7 June 2018
Accepted 9 June 2018
Available online 10 June 2018

Keywords:
Parabens
Water
Urine
Dispersive magnetic solid phase extraction
Gas chromatography–mass spectrometry

ABSTRACT

This study describes the use of a magnetic multi-walled carbon nanotube composite for the preconcentration of nine parabens (methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, phenyl and benzylparaben) from water and urine samples after in situ acetylation. The enriched extracts were obtained by dispersive magnetic solid phase extraction (DMSPE) and analysed by gas chromatography with mass spectrometry (GC–MS). Several parameters affecting the adsorption (extraction time, magnetic material mass and ionic strength) and desorption (desorption solvent nature and volume, and desorption time) DMSPE steps were investigated. Matrix-matched calibration was recommended for quantification of the samples. Linearities in the 0.5–150 ng mL^{-1} range were obtained, depending on the compound. Under the optimal experimental conditions, the limits of detection ranged between 0.03 and 2.0 ng mL^{-1}, depending on the sample matrix and the paraben congener. None of the samples analysed contained the above mentioned parabens. The method was validated with two water samples (harbour and wastewater treatment plant) and two urine samples spiked at two concentration levels. Recoveries in the 81–119% range were obtained.

1. Introduction

Parabens are alkyl esters derived from p-hydroxybenzoic acid (PHBA), catalogued as being lipophilic, inert, odourless, tasteless, colourless and stable over a wide pH range [1]. These compounds show antimicrobial and antifungal properties, since they can disrupt the cell membrane and intracellular proteins, and affect the enzymatic activity of microbial cells. They are widely used as preservatives in a wide variety of products such as cosmetics, food and drugs [2]. An increase in the length of the alkyl chain increases the antimicrobial activity but decreases water solubility. For this reason, these compounds are generally applied as mixtures, methylparaben (MeP), ethylparaben (EtP), propylparaben (PrP) and butylparaben (BuP) being the most commonly used congeners [3,4].

Parabens have long been considered as safe preservatives because of their high absorption rate, rapid metabolization to PHBA and excretion. A low level of endocrine disrupting activity has also been associated to them, as has the appearance of breast cancer [1–3]. Insofar as the usual applications of parabens are concerned their main adsorption pathways are the skin and the digestive tract. Skin permeation generally decreases with increasing paraben chain length. The main metabolite of parabens is PHBA, which is excreted in urine and bile in the form of its glycine conjugate of p-hydroxyhippuric acid (PHHA). Because PHBA and/or PHHA measurements do not differentiate the paraben congener previously present in the human body, and considering the different toxicity levels of the family congeners, the monitoring of non-metabolized parabens in urine is of great importance [5–7].

Parabens in surface waters have been reported in the literature at concentrations of up to 400 ng L^{-1} depending on the compound, and at lower levels in effluents. The use of these compounds as preservatives in cosmetics has led to their appearance in seawater and swimming pools, in the latter case also as chlorinated by-products. Consequently, parabens are considered as emerging pollutants [8,9]. To date, the maximum residue level for parabens

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☆ Selected paper from the 15th Instrumental Analysis Conference, 3–5 October 2017, Barcelona, Spain.

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https://doi.org/10.1016/j.chroma.2018.06.025

has only been set for finished cosmetic products: a maximum concentration for single esters of 0.4% w/w and 0.8% w/w for mixtures of esters, in both cases expressed as acid [10–12]. Of note is the fact that the use of PrP and BuP in cosmetic products for children under 3 years is forbidden [13].

The analytical methodology applied for the determination of parabens in different matrices has been reviewed [2–49,14]. Even though the physical properties of these chemicals, mainly their high polarity and low volatility, mean that they are usually determined by liquid chromatography (LC), the availability of rapid and easy to apply derivatization reactions permits their separation by gas chromatography (GC). However, the low levels expected in environmental and biological samples make it necessary to include preconcentration steps in the analytical procedure. Classic extraction/preconcentration procedures, such as solid-phase extraction (SPE) [15–20], have been replaced by miniaturized techniques which are quicker, easier to apply, cleaner and involve low solvent consumption. The use of a solid material as extractant phase in miniaturized procedures has been proposed for parabens preconcentration. These include different techniques such as solid phase microextraction (SPME) [21–26], stir bar sorptive extraction (SBSE) [27–30], stir cake sorptive extraction (SCSE) [31], bar adsorptive microextraction (BAμE) [8,32,33], matrix solid-phase dispersion (MSPD) [34], microextraction by packed sorbents (MEPS) [5,15] and dispersive magnetic solid phase extraction (DMSPE) [35–44].

In the present investigation, a magnetic multi-walled carbon nanotube (Fe_3O_4@MWCNTs) composite is used as sorbent material for the first time for the DMSPE preconcentration of nine parabens (MeP, EtP, PrP, BuP, isopropyl (iPP), isobutyl (iBuP), pentyl (PP), phenyl (PhP) and benzylparaben (BzP)), before their determination by GC with mass spectrometry (MS), in urine and water samples. In addition, to the best of our knowledge there are no previous reports dealing with the determination of iBu, PP, PhP and BzP by DMSPE.

2. Experimental

2.1. Chemicals and solutions

Benzylparaben (benzyl 4-hydroxybenzoate, 99%, BzP), phenylparaben (phenyl 4-hydrobenzoate, 99%, PhP), pentylparaben (pentyl 4-hydroxybenzoate, 99%, PP), isobutylparaben (isobutyl 4-hydroxybenzoate, 97%, iBuP), butylparaben (butyl 4-hydroxybenzoate, >99%, BuP), isopropylparaben (isopropyl 4-hydroxybenzoate, 99%, iPrP), propylparaben (propyl 4-hydroxybenzoate, >99%, PrP), ethylparaben (ethyl 4-hydroxybenzoate, 99%, EtP), methylparaben (methyl 4-hydroxybenzoate, 99%, MeP) and 4-hydroxyacetophenone (internal standard, 99%, IS) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Stock solutions of individual analytes and the IS were prepared in methanol at 1000 mg L^{-1} from commercial substances and stored in the dark at −20 °C. Working solutions containing all the compounds at 10 mg L^{-1} were prepared daily in water and stored at 4 °C.

Iron chloride (III) (>99%), sodium chloride (>99.5%), ammonium sulfate, ammonium iron(II) sulfate hexahydrate, ammonia solution, acetic anhydride (>99%, AA) and anhydrous dibasic potassium phosphate (>99%) were purchased from Sigma-Aldrich. MWCNTs with average diameters between 40 and 60 nm, average length of >5 μm and a specific surface area of 40-70 m^2 g^{-1} were supplied by Shenzhen Nanotech Port Co., Ltd. (Guangdong Sheng, China). Methanol (>99.9%), ethanol and ethyl acetate (99.8%) were obtained from J.T. Baker (Deventer, The Netherlands). Other reagents used for the synthesis of sorbents were: aniline (99.5%) pyrrole (98%), oleic acid (99%), (3-aminopropyl)triethoxysilane (98%, APTS), chitosan (medium molecular weight), dopamine hydrochloride and styrene (99%); all of them were purchased from Sigma-Aldrich. Distilled water was purified using a Milli-Q system (Millipore, Bedford, MA, USA. Helium (Air Liquide, Madrid, Spain) was used as carrier gas in gas chromatography.

Table 1
Retention time and target and qualifier ions for the parabens.

Compound	t_R (min)	Target ion (*m/z*)	Q_1 (%)	Q_2 (%)
IS	10.12	121	136	–
MeP	10.47	121	152 (58)	–
EtP	11.70	121	166 (46)	138 (39)
iPrP	12.32	121	138 (74)	180 (42)
PrP	13.84	138	121 (91)	180 (25)
iBuP	15.32	121	138 (98)	107 (20)
BuP	16.34	138	121 (66)	107 (14)
PP	18.17	138	121 (54)	139 (28)
PhP	20.84	121	163 (46)	–
BzP	22.10	121	91 (47)	202 (5)

Values in brackets represent the qualifier-to-target ion ratios in percentage.

2.2. Instrumentation

An Agilent gas chromatograph (Waldbronn, Germany) 6890 N model, equipped with a split-splitless injector operated at 250 °C by injecting 2 μL in splitless mode, was used. Separation was carried out using an HP-5MS (5% diphenyl–95% dimethylpolysiloxane, Agilent) capillary column (30 m x 0.25 mm, 0.25 μm film thickness) applying a constant helium flow-rate of 1 mL min^{-1}. The oven temperature started at 80 °C for 0.1 min, was increased to 120 °C at 30 °C min^{-1} and maintained for 4 min. Next two ramps of 10 °C min^{-1} were applied, first up to 170 °C (4 min) and then up to 265 °C. Finally, a ramp of 30 °C min^{-1} was applied up to 280 °C, which was maintained for 1.5 min. The chromatographic run took about 26 min. An Agilent 5973 quadrupole mass spectrometer, equipped with an inert electron impact ionization source operating at 70 eV, was used for detection purposes. Temperature values of 230, 250 and 150 °C were set in the ion source, transfer line and quadrupole, respectively.

Retention times of the compounds are shown in Table 1. The analytes were quantified in the selected ion monitoring mode (SIM) using the target and one or two qualifier ions (Table 1). Identification of the parabens was carried out by injection of pure standards, diluted at 1 μg mL^{-1} concentration level, and comparison of the retention time and scan mass-spectra for each one.

Samples were filtered with PVDF filters (0.45 μm) (Teknokroma, Barcelona, Spain). An EBA 20 (Hettich, Tuttlingen, Germany) centrifuge, used at the maximum speed (6000 r min^{-1}), and an IKA-KS 130 Basic orbital stirrer (IKA, Staufen Germany) were used for sample treatment. Permanent magnets composed of Nd-Fe-B were supplied by Supermagnete (Gottmadingen, Germany). The magnets were blocks (50 × 15 x 15 mm and 86 g weight) with a strength of 33 kg. Evaporation of the sample extracts was carried out on an XcelVap^{TM} Evaporation System (Horizon Technology, Salem, USA).

2.3. Synthesis of Fe_3O_4@MWCNTs composite

The magnetic material was synthesized according to the procedure previously reported by Asgharinezhad and Ebrahimzadeh [45]. To this purpose, the MWCNTs were purified by dispersion in a 1 mol L^{-1} HNO_3 solution for 6 h at room temperature, washed for several times with distilled water and finally dried at 100 °C. Next, 0.5 g of the purified MWCNTs were suspended in 250 mL of a solution containing 0.85 g $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ and 0.422 g $FeCl_3$ at 50 °C. The suspension was submitted to ultrasounds for 20 min and Fe_3O_4 precipitated on the MWCNT walls by adding dropwise 20 mL of 8 mol L^{-1} ammonia solution, while the mixture was continuously