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Trace analysis of parabens, triclosan and related chlorophenols in water by headspace solid-phase microextraction with in situ derivatization and gas chromatography–tandem mass spectrometry

Jorge Regueiro[a], Elias Becerril[a,b], Carmen Garcia-Jares[a], Maria Llompart[a,*]

[a] Departamento de Quimica Analitica, Nutricion y Bromatologia, Instituto de Investigacion y Analisis Alimentarios, Universidad de Santiago de Compostela, Santiago de Compostela 15782, Spain
[b] Universidad Nacional Autonoma de Mexico, Instituto de Ingenieria, Ciudad Universitaria, 04510 Mexico, D.F., Mexico

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ABSTRACT

An in situ derivatization solid-phase microextraction method has been developed for the determination of parabens, triclosan and related chlorophenols in water. Acetylated derivatives are selectively determined using gas chromatography with tandem mass spectrometry. Parameters affecting both derivatization and SPME procedures, such as fiber coating, extraction mode, temperature, volume of derivatizating reagent and ionic strength, are studied and optimized through a multifactorial experimental design. The performance of the method is studied in terms of accuracy, linearity, precision and limits of detection. Quantitative recoveries (≥82%) and satisfactory precision (RSD ≤ 12%) are obtained. Limits of detection at the low picogram per millilitre level are achieved for all target compounds. Linearity is studied in a wide range of concentrations and an analysis of variance with a lack-of-fit test is run to validate the calibration data. Extraction time profiles are also obtained. Finally, the applicability of the proposed method is demonstrated for several real samples including river water, wastewaters and swimming pool water. Since no matrix effects are observed, quantification can readily be carried out by external calibration with ultrapure water standards.

1. Introduction

The spectrum of pollutants produced and released into the environment has increased over the past 15 years. Among these compounds, labelled as emerging contaminants, personal care products (PCPs) have gathered increasing interest in recent years. This group of emerging pollutants encompasses a wide range of chemicals, including several phenolic compounds such as triclosan (TCS) and the esters of *p*-hydroxybenzoic acid, commonly known as parabens. They are extensively employed as antimicrobial and preservative agents in a variety of consumer products such as deodorants, bath gels, shampoos, creams and tooth pastes [1–4]. Parabens are also used as preservatives in pharmaceuticals, as well as in food and beverage processing.

Urban wastewater constitutes one of the main sources of these compounds in the environment and, although many of them are removed in a considerable extension during conventional sewage treatment plant (STP) processes [5–7], they have been detected in river water [8–10].

For most of them, ecotoxicological data are still scarce and therefore, it is difficult to predict what health effects they may have on humans and aquatic organisms. Although the acute toxicity of these compounds is supposed to be low, parabens can act as weak endocrine disrupter chemicals (EDCs) [11,12] and triclosan can be converted, under certain conditions, into more toxic and persistent compounds, such as chlorophenols, dioxins or methyl triclosan [13–15].

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.

Few methods have been reported for the determination of parabens in water samples. Most of them rely on the use of solid-phase extraction (SPE) followed by liquid chromatography (LC) [16] or gas chromatography (GC) with mass spectrometry (MS) detection [5,17]. Recently, a method based on solid-phase microextraction (SPME) and gas chromatography coupled to tandem mass spectrometry (GC–MS/MS) has also been reported [18].

Regarding triclosan and related phenols, SPE is again the most common extraction technique, previously to their determination by gas or liquid chromatography [14,19]. New approaches based on microextraction techniques have recently been reported. Thus, triclosan has been extracted from water samples using SPME

* Corresponding author. Tel.: +34 981563100x14225.
E-mail address: maria.llompart@usc.es (M. Llompart).

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[20], stir bar sorptive extraction (SBSE) [21], hollow-fiber liquid-phase microextraction (HF-LPME) [22] and dispersive liquid–liquid microextraction (DLLME) [10]. All these techniques allow eliminating the disadvantages of conventional extraction methods, such as solvent and time consumption, while achieving low limits of quantification.

Due to their polar nature, these compounds are often derivatized for GC analysis to reduce their adsorption in the chromatographic system, improving sensitivity, peak separation and peak symmetry [19,23]. Although analytical derivatizations are effective, they usually involve additional steps, which increase even more the time required for sample preparation.

An on-fiber silylation procedure using *N*-methyl-*N*-(*tert.*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) has been applied for derivatization of parabens and triclosan after SPME from water samples [18,20]. The same silylating reagent has been recently employed for the determination of triclosan in water using a simultaneous derivatization and extraction by DLLME [10]. Pentafluoropropionic acid anhydride (PFPA) has also been used to form pentafluoropropionyl derivatives of endocrine disrupter phenols and acids, including triclosan and parabens [5].

In situ acetylation with acetic anhydride is one of the most common derivatization procedures for phenolic compounds [24,25]. This reaction can be performed in aqueous samples, in a few minutes, with high efficiency and using low-cost reagents, much more comparing with silylating agents. Acetylation has been successfully used in the determination of triclosan in water samples using a HF-LPME method [22].

The aim of the current work is to develop a method based on SPME with in situ acetylation and GC–MS/MS for the analysis of parabens, triclosan and related phenols in water samples. The target analytes are extracted from aqueous samples after an in situ derivatization step to obtain their corresponding acetyl derivatives. The use of MS/MS detection is expected to increase the selectivity of the determinations for complex matrices, such as STP wastewaters, decreasing the quantification limits of the proposed method.

A multifactorial experimental design is performed to evaluate and optimize main experimental parameters potentially affecting the microextraction and derivatization processes. Accuracy, precision, linearity and detection limits (LODs) are evaluated to assess the performance of the proposed method. Several environmental water samples, including wastewaters, are analyzed to demonstrate the applicability of the proposed method.

2. Experimental

2.1. Reagents and materials

Methyl-4-hydroxybenzoate (methylparaben, MP), ethyl-4-hydroxybenzoate (ethylparaben, EP), propyl-4-hydroxybenzoate (propylparaben, PP), butyl-4-hydroxybenzoate (butylparaben, BP), 2,4,6-trichlorophenol (2,4,6-TCP) and 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan, TCS) were purchased from Aldrich (Milwaukee, WI, USA). Table 1 shows the Chemical Abstracts Service (CAS) registry numbers, molecular weights, octanol–water partition coefficients ($\log K_{ow}$) and chemical structures of the target compounds.

[2,3,5,6-$^2H_4$]Methyl-4-hydroxybenzoate (methylparaben-d_4) was obtained from C/D/N Isotopes (Quebec, Canada) whereas carbon-13 labelled triclosan ([^{13}C]TCS) was provided by Cambridge Isotope Labs. (Andover, MA, USA) as 100 μg mL^{-1} solution in nonane.

Methanol, ethyl acetate, *n*-hexane and acetic anhydride (Ac_2O) were provided by Merck (Darmstadt, Germany). Individual stock solutions of each compound were prepared in methanol. Further dilutions and mixtures were prepared in *n*-hexane and methanol. The latter were employed for spiking water samples. Working solutions were made by appropriate dilution and then stored in amber glass vials at −20 °C.

Sodium hydroxide, sodium hydrogenphosphate heptahydrate and sodium thiosulphate were purchased from Alfa Aesar (Karlsruhe, Germany). Potassium hydrogencarbonate was obtained from Aldrich and sodium chloride was provided by VWR Prolabo (Fontenay-sous-Bois, France). All solvents and reagents were of analytical grade. Ultrapure water was obtained from a Milli-Q water-purification system (Millipore, Billerica, MA, USA).

The SPME manual holders and fibers were supplied by Supelco (Bellefonte, PA, USA).

Five different commercial fiber coatings were used throughout the present work: 85 μm polyacrylate (PA), 100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 75 μm carboxen/polydimethylsiloxane (CAR/PDMS) and 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS). Prior to first use, fibers were conditioned as recommended by the manufacturer.

Different real water samples, including river water, urban wastewater and swimming pool water, were collected in amber glass containers. The excess of free chlorine in the swimming pool water sample was removed by addition of sodium thiosulphate (0.1 mg mL^{-1}). Samples were filtered through glass fiber filters (Millipore, Billerica, MA, USA) and stored in the dark at 4 °C until analysis.

2.2. Gas chromatography–mass spectrometry

The GC–MS/MS analysis was performed using a Varian 450-GC gas chromatograph (Varian Chromatography Systems, Walnut Creek, CA, USA) coupled to an ion trap mass spectrometer Varian 240-MS (Varian) with a waveboard for multiple MS (MS^n) analysis. The system was operated by Saturn GC–MS Workstation v6.9 software.

Separation was carried out on a J&W HP-5MS capillary column (30 m × 0.25 mm I.D., 0.25 μm film thickness) from Agilent Technologies (Palo Alto, CA, USA). Helium (purity 99.999%) was employed as carrier gas at a constant column flow of 1.0 mL min^{-1}. The GC oven temperature was programmed from 60 °C (held 2 min) to 200 °C at 30 °C min^{-1} (held 2 min) and then until 280 °C at 40 °C min^{-1} (held 1 min) (total analysis time = 12 min).

Splitless mode (held 2 min) was used for injection, the split flow was set at 20 mL min^{-1} and the injector temperature was kept at 240 °C.

The ion trap mass spectrometer was operated in the electron impact (EI) ionization positive mode (+70 eV) using an external ionization configuration. Manifold, ion trap, ion source and transfer line temperatures were maintained at 40, 150, 180 and 280 °C, respectively. Helium was also used as damping gas at a flow of 0.8 mL min^{-1}.

In the full scan mode the mass range was varied from 35 to 500 m/z at 0.6 s scan^{-1}. For MS/MS analysis, general parameters were as follows: filament/multiplier delay, 5 min, filament emission current, 80 μA, electron multiplier potential, 1500 V, multiplier offset, +100 V, and AGC target value, 8000 counts. Specific MS/MS conditions and retention times for each target compound are listed in Table 2. The analytes were positively identified by comparison of their mass spectra and retention times to those of standards.

2.3. Solid-phase microextraction (SPME)

Aliquots of 10 mL water sample were placed in 22 mL headspace vials, where 0.1 g sodium hydrogenphosphate heptahydrate and 3.5 g sodium chloride, as necessary for the experiment, were pre-