



Trace analysis of endocrine disrupting compounds in environmental water samples by use of solid-phase extraction and gas chromatography with mass spectrometry detection



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ABSTRACT

A novel analytical method using a continuous solid-phase extraction system in combination with gas chromatography–mass spectrometry for the simultaneous separation and determination of endocrine disrupting compounds (EDCs) is reported. The method was applied to major EDCs of various types including parabens, alkylphenols, phenylphenols, bisphenol A and triclosan in water. Samples were preconcentrated by using an automatic solid-phase extraction module containing a sorbent column, and retained analytes eluted with acetonitrile for derivatization with a mixture of *N,O*-bis(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane. A number of variables potentially influencing recovery of the target compounds such as the type of SPE sorbent (Silica gel, Florisil, RP-C₁₈, Amberlite XAD-2 and XAD-4, Oasis HLB and LiChrolut EN), eluent and properties of the water including pH and ionic strength, were examined. LiChrolut EN was found to be the most efficient sorbent for retaining the analytes, with ~100% efficiency. The ensuing method was validated with good analytical results including low limits of detection (0.01–0.08 ng/L for 100 mL of sample) and good linearity ($r^2 > 0.997$) throughout the studied concentration ranges. The method exhibited good accuracy (recoveries of 90–101%) and precision (relative standard deviations less than 7%) in the determination of EDCs in drinking, river, pond, well, swimming pool and waste water. Waste water samples were found to contain the largest number and highest concentrations of analytes (3.2–390 ng/L)

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1. Introduction

Endocrine disrupting compounds (EDCs) are exogenous substances that alter some function of the endocrine system and have adverse health effects on intact organisms, their offspring or (sub)populations as a result. EDCs mimic or block the action of natural hormones, and hence biological functions in living organisms, thus leading to impaired reproduction, growth and development. These compounds can enter waterways through many routes including: direct discharge into water; use of pharmaceuticals and chemicals by householders, farmers and industries; accidental spills and release of compounds; and also indirectly, through diffuse sources such as storm water runoff [1,2]. Some structurally diverse EDCs are present in a large variety of products commonly used in daily life including detergents, personal care products (e.g., cosmetics), pharmaceuticals and industrial formulations [3]. The US EPA Endocrine Disruptor Screening Program

was launched to develop official screening methods and toxicity testing strategies for approximately 87,000 compounds [4]. Alkylphenolic compounds have been included on several EDC lists owing to their estrogenic activity. Thus, nonylphenol (NP) and 4-*tert*-octylphenol (4OP) are listed as priority hazardous substances in European Community Water Framework Directive 2000/60/EC and in Final European Union (EU) decision No. 2455/2001/EC [5]. EC has set a maximum allowable concentration of nonylphenol of 0.3 µg/L in inland and other surface waters, and 0.1 or 0.01 µg/L as maximum annual average concentration of octylphenol in inland and other surface waters, respectively [6]. Other EDCs of relevance to water quality control include bisphenol A (BPA, which is used mainly in the production of polycarbonate plastics and epoxy resins), and parabens, and triclosan, which are extensively used as preservatives and disinfectant (usually in mixtures) in a wide range of products including cosmetics and toiletries (e.g., shampoos, soaps, skin care formulations, toothpastes) [7]. Developing accurate methods for determining these contaminants is therefore of great interest.

Most available analytical methods for determining parabens or alkylphenols in environmental water samples require some

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pretreatment to obtain a sample fraction enriched with all target analytes and as free as possible of other matrix components [8]. A number of sample preparation techniques including liquid–liquid extraction [9], single-drop microextraction [10], dispersive liquid–liquid microextraction [11], solid-phase extraction (SPE) [12], solid-phase microextraction [13,14] and stir-bar sorptive extraction [7,15] have been used to extract and concentrate contaminants from water samples. SPE is the preferred choice as it is especially well suited to multi-residue analysis of compounds spanning a wide range of polarity or possessing diverse physico-chemical properties [16]. The SPE technique is usually implemented by using a small column or cartridge containing an appropriate sorbent. Oasis HLB (divinylbenzene/*N*-vinylpyrrolidone copolymer) has been commonly used as SPE sorbent for triclosan (TCS), alkylphenols and BPA [17–19]. Also, LiChrolut EN (an ethinylbenzene–divinylbenzene copolymer) has been used for some EDCs such as alkylphenols, BPA, TCS and parabens [8,20]. Octadecyl bonded silica (C18) cartridges have been used for the SPE of pharmaceutical products, and phenolic endocrine disrupting chemicals including BPA, TCS, NP, nonylphenol monoethoxylate and nonylphenol diethoxylate from waste water and sewage sludge samples [21,22]. Other types of sorbents such as Bond Elut and Strata-X have been used for SPE of alkylphenols and BPA in environmental water samples [12,23].

Some of the most frequently used methods for analysis of parabens, BPA, TCS and alkylphenols are based on liquid chromatography with ultraviolet [24], mass spectrometry (MS) [21] or tandem mass spectrometry (MS/MS) detection [25,26]. By contrast, gas chromatography (GC) is the most widely used technique for determining analytes in combination with flame-ionization [11], MS [10,17,18] or MS/MS detection [13,27]; however, the polar nature of the analytes requires their derivatization in order to reduce adsorption on the chromatographic column or thermal decomposition of the analytes in the injector port, and improve sensitivity and peak separation as a result. Various derivatization methods including acetylation, alkylation and silylation have been used for the GC analysis of BPA, alkylphenols and triclosan in water samples. Derivatization reagents for EDCs typically include acetic anhydride [7,13,15], trifluoroacetic anhydride [9], pentafluorobenzoyl chloride [20] and pentafluoropropionic anhydride (PFPA) [28]. However, the most common choice continues to be silylation reagents, especially for low-volatility polar compounds such as EDCs. *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) [27], *N,O*-bis(trimethylsilyl)acetamide (BSA) [10], *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) [29,30] and mixtures of BSTFA and 1% trimethylchlorosilane (TMCS) [17,18] or *N*-*tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA) with 1% *tert*-butyldimethylchlorosilane (TBDMSCl) [31] have been widely used to derivatize alkylphenols, BPA and parabens in environmental water samples.

Most available methods for determining EDCs in water samples only encompass one or two groups of compounds of similar polarity, structure or activity. The primary aim of this work was thus to develop a sensitive method for the simultaneous determination of different types of EDCs (alkylphenols, phenylphenols, BPA, parabens and TCS) in also different types of environmental water. To this end, the sample preparation step was automated by using a continuous SPE system. After elution, the target analytes were manually derivatized prior to GC with MS detection. The effect of operational variables influencing the yield of the derivatization reaction and the extraction efficiency of the automatic SPE system were optimized. The ensuing method was assessed for analytical performance and potential applications to real samples investigated.

2. Experimental

2.1. Chemical reagents and materials

The chemicals used as analyte standards and reagents were all reagent-grade or better. Standards of the parabens [methylparaben (MeP), ethylparaben (EtP), propylparaben (PrP), butylparaben (BuP), isopropylparaben (iPrP), isobutylparaben (iBuP) and benzylparaben (BzP)], phenylphenol [2-phenylphenol (2PH) and 4-phenylphenol (4PH)], alkylphenols (NP and 4OP), BPA, and TCS were supplied from Sigma–Aldrich (St. Louis, USA). The most salient properties (pK_a and $\log K_{o/w}$) of the target compounds are shown in Table 1. Derivatizing reagents (BSA, BSTFA, TMCS, acetic anhydride and PFPA), hydrochloric acid (reagent-grade, 37%), potassium hydroxide, potassium nitrate, potassium carbonate and triphenylphosphate (internal standard, IS) were supplied by Fluka (St. Louis, USA). Chromatographic grade solvents (methanol, ethanol, 2-propanol, ethyl acetate, acetonitrile, acetone, petroleum ether, dichloromethane and *n*-hexane) were purchased from Merck (Darmstadt, Germany). All products were handled with care, using efficient fume hoods and wearing protective gloves. Polymeric sorbents Oasis-HLB (particle size 50–65 μm) and LiChrolut EN (particle size 40–120 μm) were obtained from Waters (Milford, USA) and Merck, respectively. Silica reversed-phase sorbent with octadecyl functional groups (RP-C18, particle size 40–63 μm), Silica Gel (particle size 15–35 μm), Florisil (particle size 16–30 μm), Amberlite XAD-2 (particle size 20–60 μm) and Amberlite XAD-4 (particle size 20–60 μm) were purchased from Sigma–Aldrich. The injection port liners were obtained from Thermo Electron SA (Madrid, Spain).

Standard stock solutions containing 1 g/L of each target analyte were prepared in methanol and stored in glass-stopped bottles at 4 °C in the dark. Standard working-strength solutions were prepared by sequential dilution of each standard with water previously purified passage through a Milli-Q System from Millipore (Bedford, MA) and adjusted to pH ~ 4.0.

2.2. Instruments and apparatus

Analytes were determined by GC–MS on a Focus GC instrument interfaced to a DSQ II mass spectrometer and controlled by a computer running XCalibur software (Thermo Electron SA). The GC column was a 30 m \times 250 μm i.d. DB-5MS capillary column with film thickness of 0.25 μm (J & W, Folson, CA, USA). The carrier gas used was ultrapure helium at a flow rate of 1.2 mL/min (purity 6.0; Air Liquide, Madrid, Spain). The column oven temperature program involved an initial temperature of 70 °C for 1 min; an increase at 14 °C/min to 150 °C; then an increase at 6 °C/min to 215 °C, an increase at 10 °C/min to 285 °C. The injector, transfer line and ion source temperature were 285, 280 and 200 °C, respectively; and the time for solvent delay was set at 8 min. The mass spectrometer was operated in selected ion monitoring mode (SIM) for the quantification of analytes after electron ionization (70 eV). The mass range from 60 to 400 amu was considered in full scan analysis. For each silyl derivative, M^{*+} , $[M-15]$, and other additional ions were monitored which are included in Table 1, where M^{*+} is the molecular mass and $[M-15]$ is the molecular mass minus 15 corresponding to the loss of a CH_3^{\bullet} of the $\text{Si}(\text{CH}_3)_3$ group.

The continuous SPE system was assembled from a Gilson Minipuls-3 peristaltic pump (Villiers-le-Bel, France) fitted with poly (vinylchloride) tubes, two Rheodyne (Cotati, CA, USA) 5041 injection valves, PTFE (3 mm i.d.) laboratory-made columns of different lengths packed with each sorbent material. In order to avoid abrupt changes in column compactness when LiChrolut EN or Oasis HLB sorbents were soaked, each sorbent segment (1.0 cm long) was separated by one segment of an inert material (i.e., PTFE

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