Journal of Chromatography A, 1218 (2011) 3837–3844

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Stir bar sorptive extraction of parabens, triclosan and methyl triclosan from soil, sediment and sludge with *in situ* derivatization and determination by gas chromatography–mass spectrometry

Ana María Casas Ferreira[a,*], Monika Möder[b], M.E. Fernández Laespada[a]

[a] *Departamento de Química Analítica, Nutrición y Bromatología. Facultad de Ciencias Químicas, Universidad de Salamanca, 37008 Salamanca, Spain*
[b] *Helmholtz Centre for Environmental Research - UFZ, Permoserstrasse 15, D-04318 Leipzig, Germany*

ARTICLE INFO

Article history:
Received 16 March 2011
Received in revised form 14 April 2011
Accepted 17 April 2011
Available online 28 April 2011

Keywords:
Stir bar sorptive extraction
In situ derivatization
Endocrine disruptor compounds
Soil samples

ABSTRACT

The aim of this research work was the evaluation of stir-bar sorptive extraction (SBSE) in combination with an *in situ* derivatization to determine parabens (methylparaben, isopropylparaben, n-propylparaben, butylparaben and benzylparaben), triclosan and methyltriclosan in soil samples. This is the first time that this approach has been applied to the determination of these compounds in soil samples, providing important advantages over conventional extraction techniques, such as minimization of sampling handling, complete elimination of the use of organic solvents and simplification of the analytical procedure with reduced time consumption. The enriched target analytes were desorbed thermally using a thermodesorption system coupled to a gas chromatograph and a mass spectrometer. The optimized derivatization and SBSE extraction conditions, as well as the analytical characteristics of the method were obtained using spiked soil samples. The proposed methodology proved to be easy to use and sensitive, with limits of detection between 80 ng/kg and 1.06 μg/kg, and reproducibility values below 13%. The accuracy of the method was evaluated at two concentration levels, obtaining apparent recoveries between 91% and 110%. The matrix composition significantly influenced the extraction procedure, and a need to adopt a standard additions protocol is apparent. The analytes assayed were determined successfully in different environmental soil samples.

1. Introduction

Stir bar sorptive extraction (SBSE) is a solventless sampling technique introduced by Baltussen et al. [1] to extract organic analytes from environmental samples by sorption onto polydimethylsiloxane (PDMS) coated stir bars (so-called twisters^{TM}) [2]. The analytes are recovered thermally and analyzed on-line by gas chromatography (GC) [3]. Additionally liquid desorption can be combined with classical GC and liquid chromatography (LC) [4]. Large volume injection is often applied in order to obtain the highest possible sensitivity [4]. For complete transfer of the sorbed fraction into the analytical system, thermal desorption is preferred.

SBSE has mainly been used for the analysis of different types of contaminants in aqueous samples, with hundreds of applications in the literature [5–10], and it is also possible to find applications for the determination of organic compounds in biological fluids [11–15] and in food matrices [16–19].

For the analysis of soil samples with SBSE, most applications reported require a previous extraction step with techniques such as ultrasonic solvent extraction (USE) [20,21], pressurized liquid extraction (PLE) [22], or pressurized subcritical water extraction (PSWE) [23]. The extract, previously diluted in water, is subjected to the SBSE extraction process. Few references are available concerning the extraction of pollutants by the twister directly in the soil sample. To the best of our knowledge, only Tan et al. [24] have analyzed a range of endocrine disrupting compounds (EDCs) in biosolids and sludge samples, using SBSE directly in solid samples.

Esters of p-hydroxybenzoic acid (parabens) and 2-(2,4-dichlorophenoxy)-5-chlorophenol (triclosan) are compounds with bactericidal and antimicrobial properties and are mainly employed in the formulation of personal care products (PCPs) such as toothpaste, deodorants, beauty creams, solar filters, and bath gels [25]. In addition, parabens are added to canned foods and beverages as preservatives. Triclosan is also incorporated as a biocide in sports clothes, footwear, carpets, plastic toys and kitchenware [26]. Methyl triclosan is a transformation product of triclosan formed for instance during wastewater treatment [27]. These compounds are known as endocrine disrupting contaminants (EDCs), and several authors have reported their estrogenic activity [28–31].

---

[*] Corresponding author. Tel.: +34 923 294483; fax: +34 923 294483.
E-mail address: anacasas@usal.es (A.M.C. Ferreira).

0021-9673/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2011.04.055

Few works have addressed the analysis of these compounds in environmental matrices. Their presence has been confirmed in aqueous matrices [32–34], although there are also publications dealing with air [35] and dust [36] samples.

Considering that wastewater is increasingly being reused for irrigation, reliable methods for their analysis in soils are required. Nuñez et al. have proposed the analysis of parabens using ultrasonic-assisted extraction [37] or molecularly imprinted polymer solid-phase extraction [38]. Nieto et al. [39] used pressurized liquid extraction for the analysis of parabens in sewage sludge. Regarding the determination of triclosan in soil samples, the techniques that have been reported previously are microwave-assisted solvent extraction (MASE) [40], ultrasonic solvent extraction (USE) [41] and pressurized liquid extraction (PLE) [42–44], all of them techniques that require the use of organic solvents and all of them time-consuming. Sánchez-Brunete et al. and González-Mariño et al. have proposed the determination of triclosan and methyl triclosan in soils and sludge samples by matrix-solid-phase dispersion (MSPD) [45,46].

Direct extraction of parabens, triclosan and methyl triclosan from soils using the SBSE method has not been reported in any previously published work. The aim of this study was to evaluate whether stir bar sorptive extraction with an *in situ* derivatization reaction can be applied successfully for the extraction and determination of these analytes directly from soils without any organic solvent. This method has the potential to reduce the sample preparation and analysis time to a considerable extent in comparison with the usual solid–liquid extractions combined with solid phase extraction (SPE) or liquid–liquid extraction (LLE) methods. Since the acetylation with acetic anhydride is used frequently for the derivatization of phenols, it was selected as *in situ* reaction for the determination of the phenolic target analytes in soil slurry [34,47,48]. Optimization of the derivatization reaction and the extraction step from soils was accomplished in order to obtain the best conditions. The enriched target analytes were desorbed thermally using a thermodesorption system coupled to gas chromatography–mass spectrometry (GC–MS).

2. Experimental

2.1. Chemicals

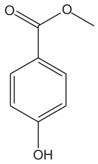
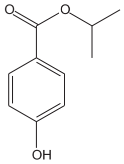
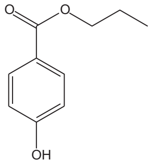
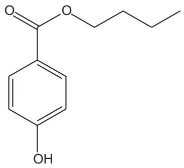
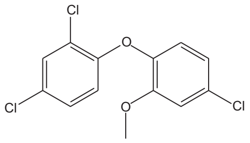
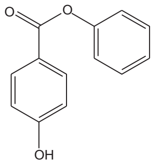
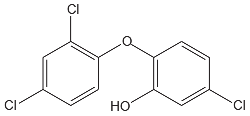
Isopropylparaben (iPrP) was supplied by TCI Europe (Zwijndrecht, Belgium). The other parabens (methylparaben (MeP), n-propylparaben (nPrP), n-butylparaben (BuP) and benzylparaben (BzP)), triclosan (TCS) and methyl triclosan (MeTCS) were supplied by Sigma–Aldrich (Steinheim, Germany). Analytical grade methanol, acetonitrile, sodium chloride as well as $NaHCO_3$ buffer salt were supplied by Merck (Darmstadt, Germany). Acetic anhydride (ReagentPlus®) was delivered by Sigma–Aldrich (Munich, Germany). The chemical structure and the octanol/water coefficients of the compounds and the retention times corresponding to the chromatographic method used are shown in Table 1.

2.2. Standard solutions and soils

2.2.1. Standard solutions

Stock solutions of all the analytes (500 mg/L in methanol) were prepared and stored at 4 °C in the refrigerator. Working solutions containing the compounds were prepared by dilution with acetone at the appropriate concentrations prior spiking the soil samples. Optimization experiments were performed using 0.5 g of soil spiked with the analytes at 100 μg/kg.

Table 1
Structural formulas, logarithm of the octanol/water coefficient, and retention times of the compounds studied.

Name	Structure	Log K_{ow}	t_R (min)[a]
Methylparaben		1.96	5.155
Iso-propylparaben		3.04	5.559
n-propylparaben		3.04	5.899
Butylparaben		3.81	6.521
Methyl triclosan		5.15	8.279
Benzylparaben		3.59	8.40
Triclosan		4.76	8.461

[a] Derivatized compounds.

2.2.2. Soil samples

Soil matrices were used to optimize the derivatization and extraction conditions and to determine the analytical characteristics of the method. Three different types of soil were chosen for the experiments: a river sediment (Leipzig, Germany), a garden soil (Norway) and a sandy soil (Leipzig, Germany). The study also included a sludge collected from a wastewater treatment plant in Leipzig, a town with about 500,000 inhabitants. The sludge was dried, sieved, and the fraction below 1 mm was collected and stored in an amber vial at 4 °C in the refrigerator until analysis. The total organic carbon (TOC), total inorganic carbon (TIC) and total carbon (TC) values shown in Table 2 of the soils and the sludge were measured using a "HighTOC II" analyser (elementar Analysensysteme, Hanau, Germany).

The spiked soil samples were prepared by adding 75 mL of a stock solution of parabens, triclosan and methyl triclosan standards