



Analysis of chlorophenols, bisphenol-A, 4-tert-octylphenol and 4-nonylphenols in soil by means of ultrasonic solvent extraction and stir bar sorptive extraction with in situ derivatisation

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ARTICLE INFO

Article history:

Received 1 March 2009

Received in revised form 8 June 2009

Accepted 12 June 2009

Available online 18 June 2009

Keywords:

Stir bar sorptive extraction

Ultrasonic solvent extraction

In situ acetylation

Phenolic pollutants

ABSTRACT

A novel method based on ultrasonic solvent extraction and stir bar sorptive extraction for the analysis of phenolic organic pollutants including chlorophenols, bisphenol-A, 4-tert-octylphenol and 4-nonylphenol in soil samples was developed. The different parameters that affect both the extraction of analytes from the soil samples, such as solvent selection, extraction time, and the partitioning from the solvent/water mix to poly(dimethylsiloxane) (PDMS) were studied. The final selected conditions consisted of the extraction of 1 g of soil with 15 mL methanol by sonication for 30 min. The methanol extract was mixed with 85 mL of Milli-Q water and extracted by means of stir bar sorptive extraction with in situ derivatisation. The stir bars were analyzed by thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS). The effects of the matrix on the recovery of the various pollutants under the developed method were studied using two soils with very different physicochemical properties. Method sensitivity, linearity, repeatability, and reproducibility were also studied. Validation and accuracy of the method were conducted by analyzing two commercial certified reference materials and by comparing the analysis of real samples with the proposed method and a classical method using pressurized solvent extraction (PSE)–GC–MS. The main advantage of this method is a substantial solvent reduction. For the extraction of only 1 g of solid sample allowing limits of detection ranging from 0.2 to 1.7 $\mu\text{g kg}^{-1}$ dw. Repeatability and reproducibility variation were lower than 20% for all investigated compounds. Results of the certified reference materials and the real samples verify the high accuracy of this method.

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1. Introduction

The presence in the environment of compounds with estrogenic and androgenic properties has become a major concern worldwide. Endocrine-disrupting chemicals (EDCs) are environmental contaminants that interfere with the function of the endocrine systems of wildlife and humans. The wide range of natural and synthetic chemicals reported to cause endocrine disruption includes some phenolic compounds. Phenolic compounds come from a wide variety of industrial sources [1], as degradation products of humic substances, tannins and lignins [2], and as degradation products of many chlorinated phenoxyacids, herbicides and organophosphorus pesticides [3,4]. Analysis of alkylphenols, chlorophenols, and bisphenol-A from environmental samples has become a subject of great interest because of their estrogenic health effects on human and wildlife. These compounds and their degradation products can be transferred to the environment at relatively high concentration

through aquatic or atmospheric systems because of their high solubility in water and the relatively high vapour pressure of some of them such as 2-chlorophenol [5–8].

Sediments or solids are good adsorbents of the phenolic contaminants due to their high surface area and surface activity. Because of their importance in the monitoring of levels in the environment, the analysis of phenolic compounds in sediment and solid samples has been extensively studied. Soxhlet extraction is one of the most popular techniques because of its simplicity and the low cost of the extraction apparatus needed. Both polar and nonpolar solvents can be used [9–13]. However, it requires a large amount of extracting solvent and a long manipulation and extraction time. Recently, pressurized liquid extraction (ASE; Dionex trade name for accelerated solvent extraction) [14–16] supercritical fluid extraction (SFE) [17,18] and microwave-assisted extraction (MAE) [19] techniques have been developed and applied to the extraction of the phenolic analytes from soil and sediment. These alternative methods allow a reduction in the extraction time and the amount of extracting solvent. Nevertheless, the extraction for large number of samples is economically limited because the equipment available in the market is expensive.

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Ultrasonic radiation is a powerful tool to speed up the analytical process in both soil [20–23] and liquid samples [24]. This method is of great help in the pre-treatment of solid samples as it facilitates operations, such as the extraction of both organic and inorganic compounds. Ultrasonic extraction is a useful, inexpensive, and efficient alternative to conventional extraction techniques and, in some cases, even to supercritical fluid and microwave-assisted extraction, as has been demonstrated for a wide range of environmental samples [25–27].

Few papers reporting extremely high sensitivity (0.1–20 ng/g) have been published using LC–MS with electro-spray ionization (ESI) or atmospheric pressure chemical ionization (APCI) [28], or LC–tandem MS–MS [29–33]. However, important signal suppression effects are frequently observed when LC–atmospheric pressure ionization (API)–MS is applied. Analytical methods, based on gas chromatography–mass spectrometry are preferred for the analysis of phenolic compounds at trace levels. In gas chromatography the polarity of some phenolic compounds results in poor chromatographic peaks, making derivatisation necessary in order to improve the peak shape and the mass spectrometry response. The most popular reagents used to make derivative compounds bearing hydroxyl groups are, *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), *N*-(tert-butyltrimethylsilyl)-*N*-methyltrifluoroacetamide (MTBSTFA) in solvent reaction, which lead to the formation of trimethylsilyl (TMS) and *t*-butyldimethylsilyl (TBS) derivatives respectively, and aqueous acetylation with acetic anhydride. Recently, many papers have been published for the analysis of phenolic compounds in various environmental samples by gas chromatography–mass spectrometry (GC–MS) technique [34–42], following extraction and derivatisation.

In a previous work by Li et al. [43] a method for phenolic compounds in soil was developed by means of acid-digested sediment suspension coupled with GC–MS. The limits obtained with this method were from 0.6 $\mu\text{g kg}^{-1}$ for bisphenol-A to 4.1 $\mu\text{g kg}^{-1}$ for pentachlorophenol. In a more recent work by Nuñez et al. [44] an ultrasonic-assisted extraction and high performance liquid chromatography–fluorescence detection was developed for the analysis of nonylphenols. In this case LODs of 60 $\mu\text{g kg}^{-1}$ were obtained by using 10 g of soil sample. Better LODs (1 ng g^{-1}) were obtained by Petrovic et al. [45] using pressurized liquid extraction (PLE) for the extraction of nonylphenols from 5 g of soil samples. Analyses were performed by means of liquid chromatography–mass spectrometry.

The use of the sorption method stir bar sorptive extraction (SBSE) with in situ derivatisation has been evaluated for the determination of phenolic compounds in aqueous samples [36]. Rodil and Popp were the first to describe a method using SBSE combined with solvent extraction to analyze micropollutants in soil samples [49]. However, to the best of our knowledge, no publication has described the use of SBSE with in situ derivatisation in the analysis of phenolic compounds in soil and sediments. The objective of this study is to develop a simple procedure for the rapid analysis of priority phenolic pollutants in soil samples by means of ultrasonic solvent extraction combined with SBSE with in situ acetylation. Soil samples were extracted with a small amount of solvent in an ultrasonic water bath. After filtration, the extract was mixed with distilled water and the solvent/water mix was extracted using a typical SBSE with in situ derivatisation procedure. Different parameters of the extraction method were evaluated such as solvent selection and the time of the ultrasonic extraction. The viability of in situ SBSE derivatisation procedure was also studied. The accuracy of the method was validated by analyzing a certified reference soil material and by comparing the results obtained with the proposed method with those obtained by using a classical pressurized solvent extraction (PSE) method.

Table 1

Main properties of the compounds.

Compounds	M.W.	Log K_{ow}	C.A.S
2-Chlorophenol	128	2.15	95-57-8
2,4-Dichlorophenol	162	3.06	120-83-2
2,4,6-Trichlorophenol	196	3.69	88-06-2
Pentachlorophenol	264	5.12	87-86-5
Bisphenol-A	228	3.32	80-05-7
4-Tert-octylphenol	206	5.28	140-66-9
4-Nonylphenol	220	5.99	104-40-5

2. Experimental

2.1. Reagents and chemicals

The four chlorophenols (1-chlorophenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; and pentachlorophenol), bisphenol-A, 4-tert-octylphenol and 4-nonylphenol (technical mix) were supplied by Aldrich Chemical (Madison, WI, USA). The main properties of these compounds are shown in Table 1. The purity of all the reference standards was always higher than 99%. A working solution containing all studied compounds at a concentration of 1 mg L^{-1} in methanol was prepared.

Acetic anhydride and sodium bicarbonate were also purchased by Aldrich Chemical (Madison, WI, USA). HPLC-grade solvents (methanol, acetone, ethanol, and acetonitrile) were purchased from Merck (Darmstadt, Germany). A certified reference material (RTC SW-846), was purchased from Resource Technology Corporation (Laramie, WY, USA).

2.2. Samples description

Different soils were analyzed to check that none of the compounds under study were present. Two different soils were finally selected for method development. Soil A was collected from an industrial area in Alicante (Spain) (organic matter 3.57%, pH 7.3, and water 16.3%) and soil B consisted of sea sediment which was collected from a Mediterranean Sea coast in Alicante (Spain) (organic matter 9.07%, pH 8.1 and water 24%). Soil samples were sieved to less than 2 mm and stored at 4 °C until use. The analysis of the blanks levels for both soils A and B gave values for all the studied compounds below the limits of detection of the method.

2.3. Preparation of spiked samples

Spiked samples were prepared using the same procedure as described in a previously published paper [46]. Each sieved (<2 mm) soil sample (10 g) was prepared by adding the corresponding working solution containing all the compounds under study at a concentration of 1 mg L^{-1} in methanol. Then, 10 mL of methanol was added and the suspension was mixed for 30 min with a mechanical shaker. After that, the bulk of the solvent was evaporated at room temperature, and the samples were stored for aging at 4 °C in stoppered conical flask for 3 days.

2.4. Ultrasonic solvent extraction

To calculate the pollutant recovery in the ultrasonic solvent extraction step, the following procedure was followed. The quantity of analyte extracted from five spiked soils following the entire extraction procedure was compared with the corresponding quantity extracted from five replicates of reference samples following the same procedure except that no soil was added in this process (to do this, the analytes were mixed in methanol in the same proportion as were the spiked soils extractions).

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