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An expeditious method for the determination of organochlorine pesticides residues in estuarine sediments using microwave assisted pre-extraction and automated headspace solid-phase microextraction coupled to gas chromatography–mass spectrometry

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ABSTRACT

Determination of organochlorine pesticides (OCPs) in sediments implicates extraction of these compounds from the matrix, which is difficult owing to strong interaction among OCPs and different constituents of the sediments, particularly organic content. The method here described is a combination of microwave assisted extraction (MAE), headspace solid-phase microextraction (HS-SPME) and gas chromatography–mass spectrometry (GC–MS), acting in selected-ion storage mode, or GC-electron capture detector (ECD, for routine analysis). Methanol was used as extracting solvent and aliquots of the MAE extracts (after inclusion of a step for sulfur elimination when required) were used to prepare aqueous solutions for HS-SPME. A complete automation of the SPME procedure increases the sample throughput, including standard addition for calibration purpose. The procedure has the advantage of exclude additional clean-up steps and pre-concentration before SPME. Application to reference sediments of different characteristics revealed absence of significant interferences from the matrix for α-lindane, γ-lindane, aldrin, dieldrin, endrin, 4,4′-DDT, 4,4′-DDD, 4,4′-DDE, heptachlor, heptachlor epoxide and good sensitivity. Detection limits ranged from 0.005 to 0.11 ng of OCP *per* gram of dried sediment using GC–MS and from 0.01 to 0.26 ng g^{-1} using GC-ECD. The linear response ranges embraced 5–6 orders of magnitude (up to 1000 ng g^{-1}) in GC–MS, being narrower for GC-ECD. The method was successfully applied to sandy and muddy sediments from Portuguese rivers estuaries, enabling quantification of seven OCPs. The method resulted effective, relatively simple and fast, being suitable for routine monitoring of residues of OCPs from sediments of different grain size and organic matter content, which influence concentration, mobility and availability of contaminants.

1. Introduction

Organochlorine pesticides (OCPs) integrate the semi volatile persistent organic compounds (POPs) that exhibit potentially harmful effects to the environment [1]. As most of the POPs, OCPs are lipophilic, persist in various media and some can be transported over long distances to regions where they have never been used [2]. OCPs can be introduced into the aquatic environment and accumulated in sediments by several pathways. As sediments are depositories of these toxic substances, owing to their low solubility and association with suspended particulate matter [3], levels of OCPs in sediments should be determined and controlled whenever possible.

Analysis of OCPs implicates extraction of these compounds from the sediment, which is difficult owing to strong interaction among OCPs and different constituents of the sediments, particularly organic content. Conventional techniques to extract low amounts of organic contaminants from complex solid matrix, like those of sediments, involve a long time consuming extraction/preconcentration procedure, which is often the limiting step of the overall analytical method. To overcome such constrain, new extraction procedures have been developed in the last years, namely microwave assisted extraction (MAE), pressurized fluid extraction (PFE), supercritical fluid extraction (SFE) and ultrasonic solvent extraction (USE) [4,5], all requiring shorter extraction time and small amount of solvent while sometimes gave higher recovery

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yields of the analytes when compared with classical extraction procedures [6]. Even so, in previous cases of MAE successful application to pre-extract OCPs from soils and sediments [7–9], the obtained extracts have needed clean-up [8,9] and/or pre-concentration [7] before analysis.

Solid-phase microextraction (SPME) has been increasingly used in the analysis of trace organic compounds, having the advantage of combining extraction and concentration in a single step [10]. Headspace (HS) SPME coupled to gas chromatography (GC) with electron capture detection (ECD) has been already applied for determination of OCPs in aqueous slurries of soil and sediments [11–13]. However, in those works the possible occurrence of sulfur in sediments, which acts as an interference, has not been considered. Additionally, the use of sediment slurries for OCPs determination by means of HS-SPME requires relatively low mass of sample aliquots [13], which may not be representative of the sediment composition, unless the sample is perfectly homogeneous. This is particularly difficult to attain in sandy sediments. As sample dilution is not possible when HS-SPME is directly applied to sediment slurries, very small aliquots of sediments have to be used in case of sediments with high levels of OCPs residues, which stresses the problem of lack of sample homogeneity and representativity. Moreover, to enhance desorption efficiency of OCPs from sediment with matrices very complex and rich in organic matter, a step of pre-extraction of the analytes is required.

Therefore, a combination of MAE and HS-SPME can be much more effective than each one of these procedures acting separately, as it permits pre-concentration of analytes at the fiber and minimizes the need of a pre-clean up of the extract from MAE, since the microextraction is performed in the headspace. Even so, the complexity of the matrix in sediments makes the identification and quantification of OCPs a difficult task. Sulfur can be an important interference as it has solubility similar to OCPs and can form co-extracts with them, causing a broad overlapping peak in gas chromatography (GC) and reducing the accuracy of quantitative measurements [14]. As reported in a recent work on pesticides determination in soil [7] which has used MAE followed by HS-SPME and GC coupled to tandem mass spectrometry (MS/MS), recovery has been found to be dependent on the type of soil due to matrix effects.

To our knowledge, a combination of MAE, HS-SPME and GC–MS has never been successfully applied before to the determination of OCPs in estuarine sediments. The method here described used precisely this combination, as well as a similar one with GC-ECD for routine analysis, with complete automation of the SPME procedure (which increases the sample throughput). To minimize matrix effects, a step for elimination of sulfur interference was included when required and standard addition was used for calibration purpose. The method resulted effective, relatively simple and fast, being suitable for simultaneous monitoring of residues of ten OCPs from sediments of different grain size and organic matter content.

2. Experimental

2.1. Reagents and solutions

Solvents and reagents were analytical grade unless further information. Methanol, Chromasolv® for HPLC, was obtained from Sigma–Aldrich (Darmstadt, Germany). The water used was deionized with conductivity <0.1 $\mu S\,cm^{-1}$. Sodium sulfite (purity 98%) and copper fine powder (purity 99.7%) for sample desulfuration were obtained from Riedel-de Haën (Seelze, Germany) and Merck (Darmstadt, Germany) respectively. Sodium chloride (purity 99.5%) was also from Merck. A mixture of eighteen OCPs (HCHs, aldrin, dieldrin, endrin, endrin ketone, endrin aldehyde, endosulfan I (α), endosulfan II (β), endosulfan sulfate, 4,4′-DDT, 4,4′-DDD, 4,4′-DDE, heptachlor, heptachlor epoxide and methoxychlor) in toluene:hexane (1:1) at concentrations of 2000 $mg\,L^{-1}$, from Supelco (Bellefonte, PA, USA), was used to prepare stock standard diluted solutions in methanol and stored at 4 °C. Working solutions of pesticides were prepared daily by appropriate dilutions with water. Reference sediments Metranal™ 16 from Analytika Ltd. (Prague, Czech Republic) and CNS300-04-100 from Resource Technology Corporation (Salisbury, United Kingdom) were used in the method validation. For decontamination, all the glass and plastic ware was washed with soap, rinsed with water, soaked overnight in 20% nitric acid aqueous solutions and rinsed with water again and methanol.

2.2. Extraction conditions

MAE was carried out using a laboratory microwave system Ethos 1 Milestone (Sorisole, Italy), provided with Teflon extraction vessels, where 10 mL of methanol and a suitable mass of sediment (ranging from 0.25 to 10 g, according to OCPs concentration) were introduced. The polydimethylsiloxane SPME fibers (PDMS, 100 μm) used were purchased from Supelco (Bellefonte, PA, USA). Fibers were conditioned in the GC injector as indicated by the manufacturer before use. For the first optimization steps, spiked aqueous solutions (10 mL) were introduced in 22 mL vials, sealed with caps and septa, thermostated, and stirred using PTFE covered magnetic stirring bars. For method validation and real sediment analysis 100 μL aliquots of MAE extracts of sediment (after centrifugation) were added to the volume of water necessary to obtain 10 mL solutions contained in 20 mL sealed vials (18 mm magnetic ultraclean closers suitable for autosampler). Real estuarine sediments were previously dried at room temperature and sieved through a screen (pore size 2 mm).

In a first optimization step the fiber was manually inserted in the GC injector. In further experiments the HS-SPME was performed using an autosampler (CTC Analytics, Combi Pal model). The optimized conditions are presented in Table 1. Blanks were processed with the samples every working day for control purposes. Unless further indication, all tests were performed in triplicate.

2.3. Chromatographic conditions

GC–MS analysis were performed by using a Varian Saturn 2000 mass spectrometer (Walnut Creek, CA) coupled to a Varian 3900 gas chromatograph equipped with a split/splitless injector port, a SPME liner (0.75 mm ID), a microseal septum system (Merlin, Half Moon Bay, CA) and a CP-Sil 8CB Low Bleed/MS (Varian) column (60 m length × 0.250 mm diameter, 0.25 μm film thickness). The carrier gas was helium of high purity (99.9995% from Air Liquide). The Varian computer software MS Workstation 6.30 controlled the GC–MS.

Table 1
SPME conditions

Extraction mode	Headspace (HS)
Fiber type	100 μm film thickness PDMS
Salting out	2 g NaCl
Pre-incubation time	30 min
Pre-incubation temperature	80 °C
Pre-incubation rotation	500 rpm[a]
Extraction time	60 min
Extraction temperature	80 °C
Extraction rotation	250 rpm[a]

[a] Rotation *per* minute.