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Optimization of the matrix solid-phase dispersion sample preparation procedure for analysis of polycyclic aromatic hydrocarbons in soils: Comparison with microwave-assisted extraction

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Abstract

A fast and simple preparation procedure based on the matrix solid-phase dispersion (MSPD) technique is proposed for the first time for the isolation of 16 polycyclic aromatic hydrocarbons (PAHs) from soil samples. Naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a*,*h*]anthracene, benzo[*g*,*h*,*i*]perylene, and indeno[1,2,3-*c*,*d*]pyrene were considered in the study. Extraction and clean-up of samples were carried out in a single step. The main parameters that affect extraction yield, such as dispersant, type and amount of additives, clean-up co-sorbent and extractive solvent were evaluated and optimized. The addition of an alkali solution in MSPD was required to provide quantitative recoveries. Analytical determinations were carried out by high performance liquid chromatography (HPLC) with fluorescence detection. Quantification limits (between 0.01 and 0.6 ng g^{-1} dry mass) were well below the regulatory limits for all the compounds considered. The extraction yields for the different compounds obtained by MSPD were compared with the yields obtained by microwave-assisted extraction (MAE). To test the accuracy of the MSPD technique, the optimized methodology was applied to the analysis of standard reference material BCR-524 (contaminated industrial soil), with excellent results.

Keywords: Polycyclic aromatic hydrocarbons; Matrix solid-phase dispersion; Microwave-assisted extraction; Soil analysis

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) comprise a group of ubiquitous environmental contaminants that originate from different emission sources, mainly associated with human activities, such as the incomplete combustion of fossil fuels, industrial processes or the use of motor vehicles. Since these pollutants exert toxic, mutagenic and carcinogenic effects, knowledge of their fate in soils is critical in hazard risk assessment [1,2].

PAHs are strongly adsorbed onto the organic fraction of sediments and soils. These compounds are mainly accumulated in the humus layer of soil, and PAHs with three or more rings tend to be strongly adsorbed. Strong sorption coupled with very low water solubility and low vapour pressures make leaching and volatilization insignificant in PAH dissipation [3].

The Spanish government has established regulatory levels for some PAHs in terms of soil uses. Maximum acceptable limits for 13 PAHs, namely: naphtalene (Naph, 1 mg kg^{-1} dm (dry mass basis)), acenaphthene (Ace, 6 mg kg^{-1} dm), fluorene (Flu, 5 mg kg^{-1} dm), anthracene (Anth, 45 mg kg^{-1} dm), fluoranthene (Flt, 8 mg kg^{-1} dm), pyrene (Pyr, 6 mg kg^{-1} dm), benz[*a*]anthracene (B[*a*]A, 0.2 mg kg^{-1} dm), chrysene (Chry, 20 mg kg^{-1} dm), benzo[*b*]fluoranthene (B[*b*]F, 0.2 mg kg^{-1} dm), benzo[*k*]fluoranthene (B[*k*]F, 2 mg kg^{-1} dm), benzo[*a*]pyrene (B[*a*]P, 0.02 mg kg^{-1} dm), dibenzo[*a*,*h*]anthracene (DB[*a*,*h*]A, 0.03 mg kg^{-1} dm) and indeno[1,2,3-*c*,*d*]pyrene (I[1,2,3-*c*,*d*]P, 0.3 mg kg^{-1} dm), have been established in soils destined for agricultural, forest and/or cattle activities [4]. The Spanish regulations are risk-oriented, in line with the European Union chemicals policy. Obviously, some aspects of the regulations are specifically tailored to the Spanish situation, such as the

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distribution of powers between the national and regional governments. However, a significant part of the approach is based on the European risk assessment protocols, and therefore, can be extrapolated at the pan-European level [5].

The analytical determination of organic pollutants, such as polycyclic aromatic hydrocarbons, in soils and sediments usually involves extensive and complex methods of sample preparation, mainly because of the difficulty in achieving a selective and quantitative leaching of the analytes from the solid sample.

Soxhlet extraction is considered as the standard method for leaching PAHs from solids, although it requires long extraction times and large volumes of organic solvents [6]. Alternatives include pressurized liquid extraction (PLE; Dionex trade name ASE for accelerated solvent extraction) [7,8] and supercritical fluid extraction (SFE) [9,10]. Although the extraction times in both PLE and SFE are short (ca. 10 min), the methods require dedicated and expensive apparatus. Other alternatives include ultrasonic-assisted extraction (USE), which is a simple and rapid method but with limited extraction efficiency [11,12], and microwave-assisted extraction (MAE) [13,14].

It has also been shown that hydrolytic treatment of soil organic matter (e.g., with methanolic potassium hydroxide) releases significant quantities of non-solvent leachable organic contaminants, which are strongly associated with and/or occluded within the soil organic matter. The release of compounds can occur in two ways. Firstly, hydrolysis of organic matter splits labile ester bonds, which results in a limited breakdown of the macromolecular humic network and improves solvent accessibility. Organic compounds that are bound to the soil organic matter by hydrolysable bonds will be released under these conditions. Secondly, the introduction of alkaline conditions causes an extension of the humic macromolecular polymeric structure as a result of mutual repulsion among negatively charged carboxyl, phenolic and hydroxyl functional groups. This provides improved accessibility within the humic macromolecular structure, promoting the release of diffusion-retarded contaminant fractions, and reducing hydrogen bonding ability, all of which combine to promote release of compounds. As a result sorbed PAHs are more accessible to the solvent and can be extracted more efficiently [15,16].

Because of the unsurprising presence of interfering compounds in the extracts, due to the complexity of the soil matrix, samples require an intensive clean-up before they can be submitted to the determination steps, which are usually carried out by gas chromatography–mass spectrometry (GC–MS) or liquid chromatography with fluorescence detection (HPLC-FLD). Solid-phase extraction (SPE) is still the most commonly used method for purification of soil and sediment extracts. A large number of sorbents are used for the isolation of organic compounds from the extract solution, including alumina, Florisil®, silica gel and many silica-based sorbents (e.g., octadecyl bonded silica (C_{18}), octyl bonded silica (C_8)) [17].

These methods are generally tedious and costly, especially when many samples must be analysed (e.g., during soil remediation projects), and a rapid a simple method is desirable. MSPD has proven to be a fast and efficient alternative to traditional extraction methods. The technique, which is based on simultaneous disruption and extraction of solid and semi-solid samples, permits complete fractionation of the sample matrix components as well as selective elution of single compounds or several classes of compounds from the same sample. The sample disperses over the surface of the bonded phase support material to provide a new mixed phase for isolating analytes from various sample matrices. Less solvent and less time are generally required than in classic methods [18,19]. The method has been most frequently applied to the isolation of drugs, herbicides, pesticides and other pollutants from animal tissues, fruits and vegetables [20,21], including isolation of PAHs from fish samples [22], honey samples [23], animal diets [24] and tissues of aquatic species [25]. However, some methods have also been successfully developed for the determination of persistent organic pollutants in other matrices such as soils, sediments, freeze-dried sludge from sewage treatment plants and indoor dust [26–28].

The aim of the present study was to optimise and validate the MSPD method, for the extraction of 16 PAHs (Naph, Ace, Flu, phenathrene (Phe), Anth, Flt, Pyr, B[*a*]A, Chry, benzo[*e*]pyrene (B[*e*]P), B[*b*]F, B[*k*]F, B[*a*]P, DB[*a*,*h*]A, benzo[*g*,*h*,*i*]perylene (B[*g*,*h*,*i*]P) and I[1,2,3-*c*,*d*]P) from soil samples. The effect of the addition of different amounts of methanolic potassium hydroxide on the extraction process was also evaluated, and the effects on the extraction of the use of different types of organic solvents and sorbents (for dispersal and as co-column) were studied. The results obtained with MSPD were compared with those obtained with the microwave-assisted extraction based method [13], and the analytical method was validated with BCR-524 (contaminated industrial soil) reference material.

2. Experimental

2.1. Reagents, standards and materials

Polypropylene SPE syringe barrels (15 mL capacity) fitted with a single bottom frit and additional 20 μm polyethylene frits were obtained from International Sorbent Technology (Mid Glamorgan, UK).

HPLC chromatographic separations were developed in a system comprising a 600E pump with a gradient controller (Waters, Milford, MA, USA), UV/Visible diode array and fluorescence detectors in series (HP Series 1100, Agilent, Waldbrom, Germany). The injector (Rheodyne Model 7725i, Cotati, CA, USA) was fitted with a 20 μL loop. Analytical column temperatures were controlled with a MetaTherm 9540 oven (MetaChem, Torrance, CA, USA). The analytical column was a 250 mm × 4.6 mm I.D. Waters PAH C_{18} column (particle size 5 μm). A Waters guard-pak, with Nova-Pak C_{18} inserts, was used to protect the analytical column (both purchased from Waters). Agilent Chemstation Software (Rev. A. 06.03 [509]) was used for data acquisition.

Elemental analyses were carried out in shared research facilities at the University of Santiago de Compostela.

A Unicen (Orto-Alresa, Madrid, Spain) centrifuge was used to centrifuge the raw sample extracts. Solvent evaporation was