



Fast method to quantify PAHs in contaminated soils by direct thermodesorption using analytical pyrolysis



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ABSTRACT

A method for polycyclic aromatic hydrocarbon (PAH) quantification, based on pyrolysis at 450 °C combined with gas chromatography coupled with mass spectrometry and flame ionization detection (Py-GC-MS/FID), was developed and compared to a conventional PAH quantification method using accelerated solvent extraction and GC-MS analyses. The PAH contents of three coking plant soils, one gas plant soil, two wood-treating facility soils and one certified reference material (CRM - BCR 524) were determined using both methods. The results obtained with both methods showed a good match, especially in the case of the CRM. The other soil samples presented higher variability which was greatly reduced by crushing the samples to lower particle size (from < 500 to < 100 μm). Higher contents of low molecular weight (LMW) PAHs were quantified with the Py-GC-MS/FID than with the conventional method, probably because of a slight cracking phenomenon occurring during the pyrolysis and/or a loss of the LMW compounds during the sample concentration required for the conventional method. Because of the limited sample preparation and the fact that no solvent was used, the pyrolysis-based method was proven to be a faster, less expensive and more environmentally friendly than the classical methods for PAH quantification in contaminated soils.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants. They have been added to the pollutants priority list at the end of the 70s because of their toxic, mutagenic and carcinogenic properties [1]. Since then, they have been monitored in many environmental matrices, including soils, surface water, groundwater and sediments. The usual methods for PAH quantification in soils and sediments require solvent extractions and are followed by molecular analyses i.e. gas or liquid chromatography (GC or LC) with various detection modes. Traditionally samples are extracted using methods based on Soxhlet [2,3] or sonication [4,5]. They require large volumes of organic solvent and are time-consuming, e.g. Soxhlet extraction takes several hours to several days, so degradation of compounds can occur during the extraction. In the 90s, extraction techniques were developed to reduce the extraction time, the solvent volume used for extraction and consequently the preparation and analysis cost [6]. Among them are microwave-assisted extraction (MAE) which use microwave irradiation causing molecular motion without changing the molecular structure [7]. The sample and the solvent are heated by the microwave energy in

closed and pressurized extraction cells allowing to reach the analyte boiling point much faster than the traditional techniques and decrease the analysis time [8]. An alternative is the CO₂ supercritical fluid extraction (SFE) which present some advantages as little amount of organic solvents is necessary, the extraction times are usually less than 1 h and the limited solvent strength reduces the need for sample clean-up before chromatographic analyses [9] but this can prevent the complete extraction of the analytes. However SFE did not become standardized as methods developed for one SFE system are difficult to transpose to others (due to important differences of technical specifications between marketed apparatus) [10] and it has been shown that PAH extraction rates obtained with SFE are strongly dependent on the matrix type and the PAH contamination level [11,12]. Even if the extractability can be increased by adding a polar organic solvent (e.g. methanol) to the fluid [9], it might not be efficient enough to extract PAHs from highly sorptive matrices [10]. The most commonly used extraction technique seems to be the accelerated solvent extraction (ASE) or pressurized liquid extraction (PLE). It consists of pumping the solvent into pressurized and heated cells containing the sample. This high pressure allows the solvent to remain in the liquid state. As for the

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SFE and MAE this extraction technique is fast and requires low solvent amount. When compared with other extraction techniques (Soxhlet, MAE, sonication, SFE) on a wide variety of samples, ASE gives equivalent or better recovery of target compounds such as petroleum hydrocarbons [13] and PAHs [6,11,14–16].

Even if the concentration step is limited with methods using extraction techniques requiring small solvent volumes (i.e. ASE, MAE and SFE), loss of volatile compounds can still occur during solvent evaporation, leading to low recovery for these molecules [16]. Moreover, depending on the sample properties additional cleaning and/or purification steps may be required to achieve satisfactory analytical results. These procedures can be time-consuming and lead to the loss of some analytes [15].

An alternative to the extraction techniques is thermal techniques, such as thermodesorption and pyrolysis. Methods based on thermal techniques present some advantages as no solvent is needed, the preparation time is limited and the analyses can be performed directly on-line. Thermal techniques are already used in methods of quantification of organic compounds from air [17–20] or water [21–23]. In these studies, the organic compounds are collected on passive sampling or concentrated using solid phase extraction. The collection devices – sorptive bar, filter, adsorption tube... – are introduced into the thermodesorption oven and heated between 250 and 300 °C allowing the trapped compounds to desorb and be directly analyzed by GC–MS or GC–FID. The potential of pyrolysis and thermodesorption to detect organic compounds in sediments [24–27] and soils [28,29] was already explored in few studies. The analyses described there were intended to screen the samples for various molecules but did not allow compound quantification.

The aim of this study was to propose a method for PAH quantification in soils based on pyrolysis and molecular analyses which is fast, environmentally friendly and economical. Indeed, the application of pyrolysis does not require any preparation (except for the sample drying and grinding) which notably reduced the preparation time and no solvent is used, all these factors decreasing significantly the analysis cost. Several soil samples, including a certified reference material (CRM), were analyzed by the proposed method and the results were compared to those obtained by classical analyses involving ASE extraction and PAH quantification by GC–MS.

2. Materials and methods

2.1. Soil samples

Seven soil samples were tested for PAH quantification using Py-GC-MS/FID, including one CRM. All tested soils were industrial soils, heavily contaminated with PAHs. Three soils originated from former coking plant soils in Neuves-Maisons (France), Homécourt (France) and Moyeuve-Grande (France), one from a gas plant in Rennes (France), two soils from wood-treating facilities located in the Midi-Pyrénées (France) and in Umeå (Sweden), and the CRM BCR-524 which is described as a contaminated industrial soil.

All soils were stored at –20 °C to prevent volatilization of low molecular weight (LMW) compounds. After collection, the gas plant, coking plant and wood-treating facility soils were quartered, freeze-dried, sieved at 2 mm and the undersize was crushed to pass through a 500 µm sieve.

2.2. Pyrolysis-gas chromatography-mass spectrometry/flame ionization detection (Py-GC-MS/FID) analyses

2.2.1. Selection of the pyrolysis temperature

The challenge in this study was to select a temperature high enough to allow the desorption of high boiling point compounds but low enough to prevent thermal cracking of the molecules and secondary aromatization reactions that can occur under a marked thermal stress

[30]. In previous studies the temperatures selected for the detection of organic compounds by Py-GC-MS or Td-GC-MS were between 280 and 350 °C. Terán et al. [27] proposed a double-shot pyrolysis to detect the organic contaminant. PAHs were not detected during the first step at 280 °C but were generated during the 600 °C step. PAHs were then all pyrolysis products of the thermal cracking of macromolecule or 280 °C was not high enough to desorb the free PAHs. In the same way, Faure et al. [24] performed successive thermodesorption at 300 °C and pyrolysis at 620 °C on river sediments in order to screen the samples for free organic compounds and molecules inherited from macromolecule thermal breakdown, respectively. When comparing the results to the ones obtained by solvent extraction, liquid chromatography fractionation and GC–MS characterization, they observed lower abundances of high molecular weight (HMW) compounds and concluded that 300 °C was not high enough to vaporize HMW molecules. According to Medina-Vera [26], on a range of tested temperatures from 180 to 900 °C, the optimal pyrolysis temperature for the screening of PAHs in sediment is 350 °C. However at such temperature HMW compounds (benzo[ghi]perylene, benz[a]pyrene and chrysene) were not always detected. From these studies it seemed that the temperature had to be set above 350 °C in order to detect HMW compounds. González-Pérez et al. [28] used Py-GC-MS to distinguish fire-impacted soils and they showed that 500 °C-pyrolysis allows detecting PAHs up to 252 g/mol in fire-impacted soils. In our previous work [31] dealing with the evaluation of mineral retention properties towards PAHs of different molecular weights (178, 202 and 252 g/mol), the behavior of PAH/mineral associations during thermodesorption was studied. When associated with silica sand (low retention properties), all the PAHs are desorbed at temperature below 300 °C but when associated with bentonite, the PAHs are desorbed between 400 and 500 °C in much lower abundance than with the silica sand mixtures and are associated with the formation of smaller units at about 500 °C corresponding to thermal cracking products of the PAHs strongly sorbed or polymerized at the bentonite surface. These results led us to select a temperature of 450 °C which seemed a good compromise between the PAH desorption temperature associated with matrices presenting high retention properties – as it can be the case in real soils – and the temperature at which the thermal cracking of the organic compounds occurs. The selected temperature (450 °C) is consistent with a pyrolysis technique. However, even if the term pyrolysis (Py) will be used throughout the rest of the document, it should be noted again that the aim of using such temperature was not to achieve thermal cracking but to allow HMW compound desorption.

2.2.2. Py-GC-MS/FID coupling

The pyrolysis were performed on a Frontier Lab Multi-shot pyrolyzer EGA/PY-3030D and a Micro Jet Cryo-Trap MJT-1030Ex installed on an Agilent GC-FID 7890B coupled with a 5977A MS detector. Injections were done in the pulsed split mode with pulsed pressure of 50 psi until 0.5 min and a split ratio of 20:1. An Agilent DB-5MS column (20 m×0.18 mm i.d.×0.18 µm film thickness) was used for the analyses. Helium was used as carrier gas at a constant flow of 1.6 mL/min. The flow was split between the FID and the MS thanks to a dean switch with a FID/MS flow separation of 1/3. Deactivated fused silica column connected the dean switch to the FID and the MS detectors. The inlet and transfer line temperatures were set at 320 and 340 °C, respectively, and the MS quadrupole and ion source were set at 150 and 230 °C, respectively. For all analyses the MS was used in the combined selected ion monitoring (SIM)/full scan mode (Table 1). The FID temperature was set at 320 °C and the air, hydrogen and makeup (He) flows were 400 mL/min, 30 mL/min and 25 mL/min, respectively.

The FID was calibrated for PAH quantification using a standard mixture of 17 PAHs (supplied by Dr. Ehrenstorfer) listed in Table 1. Pieces of glass fiber filter GF/F (Whatman) were previously washed by sonication (1 h) in a dichloromethane (DCM)/methanol bath (v/v 1/1)

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