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

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**Keywords:** Thermal desorption; Gas chromatography; Mass spectrometry; Flame ionization detection; Accelerated solvent extraction; Polycyclic aromatic hydrocarbon

## 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 matrixes, 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 CO<sub>2</sub> 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 cleanup 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 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.

**Table 1:** Quantified PAHs, their abbreviations and the targeted ions (m/z) for the selected ion monitoring (SIM) acquisition mode.

Name	Abbreviation	m/z
Naphthalene	Nap	128
Acenaphthylene	Acy	152
Acenaphthene	Ace	154
Fluorene	Fl	166
Phenanthrene	Phe	178
Anthracene	Ant	178
Fluoranthene	Flu	202
Pyrene	Pyr	202
Benz[ <i>a</i> ]anthracene	BaAnt	228
Chrysene	Chr	228
Benzo[ <i>b</i> ]fluoranthene	BbFlu	252
Benzo[ <i>k</i> ]fluoranthene	BkFlu	252
Benz[ <i>a</i> ]pyrene	BaPyr	252
Perylene	Per	252
Indeno[1,2,3- <i>cd</i> ]pyrene	Ind-1,2,3-cd-Pyr	276
Dibenz[ <i>a,h</i> ]anthracene	DBahAnt	278
Benzo[ <i>ghi</i> ]perylene	BghiPer	276

## 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 Moyeuvre-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 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) and oven-dried. They were

inserted into the stainless steel cups used for the pyrolysis and impregnated with 1  $\mu\text{L}$  of PAH solutions at nine concentrations (0.5, 1.5, 3, 6, 10, 18, 30, 50 and 100  $\mu\text{g/mL}$ ).

The cups, containing either the calibration solutions or 0.15–3 mg of samples, were put in the pyrolysis oven set at 450  $^{\circ}\text{C}$ . The temperature of the pyrolyzer interface was maintained at 320  $^{\circ}\text{C}$ . The cryo trap allowing the concentration of the compounds at the head of the column was maintained active at  $-180^{\circ}\text{C}$  for 5 min before the beginning of the GC analysis according to the following temperature program: 1 min at 40  $^{\circ}\text{C}$ , from 40 to 195  $^{\circ}\text{C}$  at 25  $^{\circ}\text{C/min}$ , a hold-time of 2 min at 195  $^{\circ}\text{C}$ , from 195 to 315  $^{\circ}\text{C}$  at 20  $^{\circ}\text{C/min}$ , from 315 to 320  $^{\circ}\text{C}$  at 5  $^{\circ}\text{C/min}$  followed by a hold-time of 3 min at 320  $^{\circ}\text{C}$ . Compound identification was confirmed by the mass spectra obtained with the MS detector in comparison with the NIST08 and Wiley database spectra.

### *2.3. Conventional analyses*

#### *2.3.1. Solvent extraction*

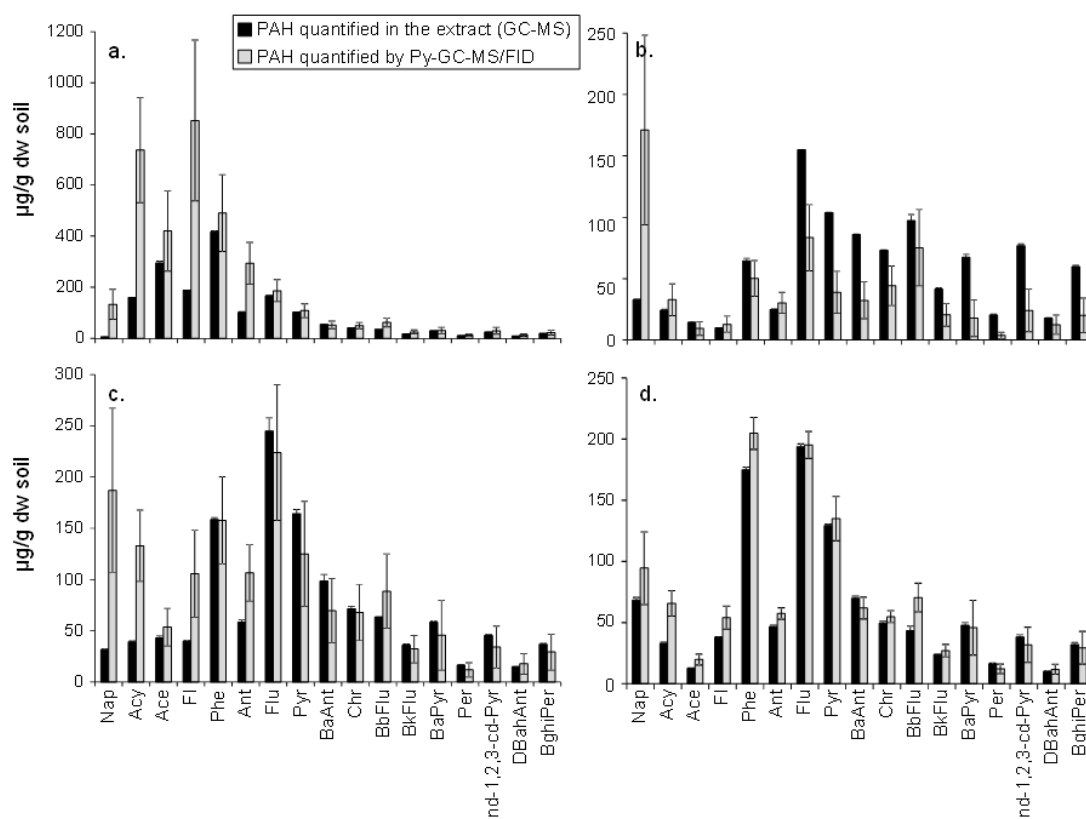
Organic matter (OM) extractions were carried out on 2 g of each sample with an accelerated solvent extractor (Dionex ASE 350). Copper powder (2 g) and sodium sulfate (2 g) were added to the extraction cells to remove the molecular sulfur and the residual water, respectively. The extractions were performed with DCM at 130  $^{\circ}\text{C}$  for 10 min and the extract volume was adjusted at 20 mL.

#### *2.3.2. GC-MS analyses*

The quantification was carried out using internal calibration. An internal PAH standard mix of [ $^2\text{H}_8$ ]naphthalene, [ $^2\text{H}_{10}$ ]acenaphthene, [ $^2\text{H}_{10}$ ]phenanthrene, [ $^2\text{H}_{12}$ ]chrysene, [ $^2\text{H}_{12}$ ]perylene, supplied by Dr. Ehrentorfer (20  $\mu\text{L}$  at 16  $\mu\text{g/mL}$ ) was added to the extractable organic matter (EOM, 80  $\mu\text{L}$ ) before being injected in GC–MS. For each quantified compounds, a calibration curve was constructed with six concentration solutions (0.3, 0.9, 1.5, 3, 6 and 9  $\mu\text{g/mL}$ ). The gas chromatograph was an Agilent 6890N, equipped with a capillary column in silica glass DB5-MS (60 m $\times$ 0.25 mm i.d.  $\times$ 0.25  $\mu\text{m}$  film thickness) coupled to an Agilent 5973 mass spectrometer in fullscan mode with a transfer line heated at 320  $^{\circ}\text{C}$ . The MS source and quadrupole temperatures were set at 230 and 150  $^{\circ}\text{C}$ , respectively. The



oven temperature program was as follow: at 70 °C for 2 min, from 70 °C to 130 °C at 15 °C/min, then from 130 °C to 315 °C at 4 °C/min and then a 30 min hold at 315 °C. The carrier gas was helium at 1.6 mL/min constant flow. The injector temperature was set at 300 °C and injections were done with 1 µL of calibration solution or EOM in splitless mode.



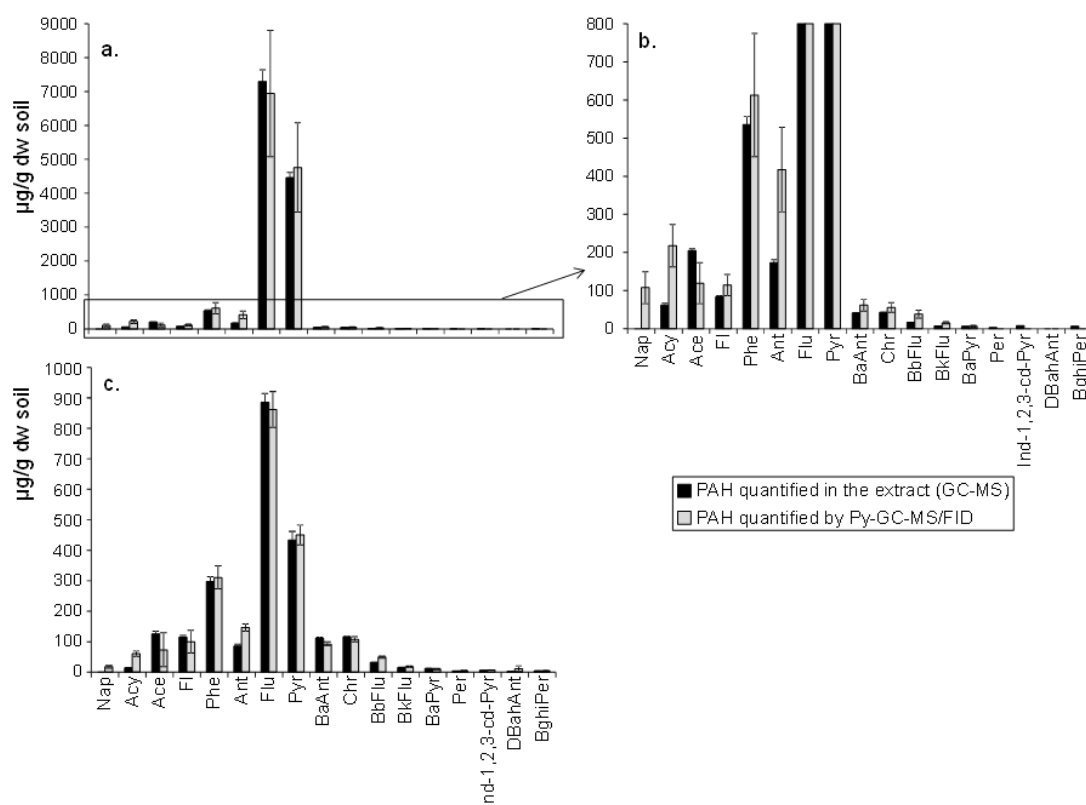
**Figure 1:** Comparison of the PAH concentrations obtained by Py-GC-MS/FID and with the conventional method for (a) the Homécourt, (b) the Neuves-Maisons, (c) the Moyeuve-Grande coking plant soils and (d) the Rennes gas plant soil crushed < 500 µm. PAH abbreviations are reported in Table 1. The error bars represent standard deviation (n=2 for the conventional method and n=5 for the Py-GC-MS/FID method).

### 3. Results and discussion

#### 3.1. Comparison between conventional and Py-GC-MS/FID quantifications

The PAHs quantified in the extract using the conventional method were compared to those quantified by Py-GC-MS/FID for the six soils (Figs. 1 and 2) and for the CRM (Fig. 3). The PAH concentrations determined by Py-GC-MS/FID for the Homécourt coking plant soil showed a satisfying correspondence with the one determined with the conventional method except for the LMW PAHs (2- and 3- ring PAHs) which were found in concentrations two to five times higher with Py-based method (Fig. 1a). These

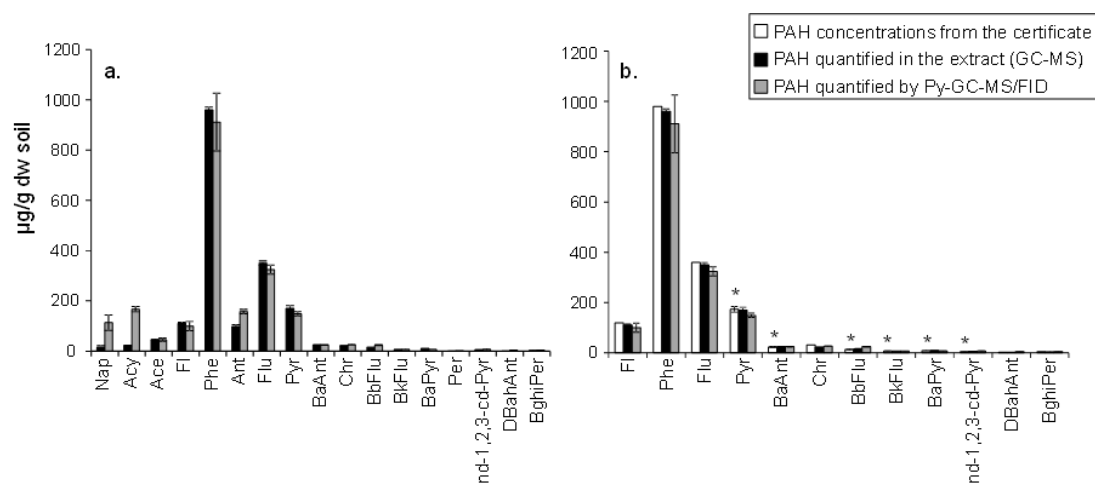
observations can also be made for the Moyeuve-Grande coking plant soil (Fig. 1c) and the Rennes gas plant soil (Fig. 1d). It was also the case for both wood-treating facility soils (Fig. 2) and the CRM (Fig. 3) but to a lesser extent as only naphthalene, acenaphthylene and anthracene, and naphthalene and acenaphthylene, respectively, were found at higher concentration with the Py-based method than with the conventional method. This higher concentration of LMW PAH obtained by Py-GC-MS/FID can be explained in two ways. First, even if the pyrolysis temperature was determined in order to avoid it, thermal breakdown of the macromolecules may have occurred, generating LMW PAHs [27]. Second, the concentration step required during the conventional method which is known to be responsible for the loss of a portion of the LMW compounds [16] led to an underestimation of the LMW PAH concentrations with the conventional method. As values for the most impacted compounds were not reported in the CRM certificate it was not possible to validate one or both hypotheses.



**Figure 2:** Comparison of the PAH concentrations obtained by Py-GC-MS/FID and with the conventional method for (a) Midi-Pyrénées wood-treating facility soil, (b) a zoomed portion of the previous graph and (c) the Umeå wood-treating facility soil crushed < 500 µm. PAH abbreviations are reported in Table 1. The error bars represent standard deviation (n=2 for the conventional method and n=5 for the Py-GC-MS/FID method).

The Neuves-Maisons coking plant soil showed important discrepancies between both quantification methods (Fig. 1b) with less PAHs quantified by Py-GC-MS/FID than with the conventional method, except for naphthalene and acenaphthylene. This sample is an aged contaminated soil known to exhibit low PAH availability [32–38] probably because of strong PAH binding with the matrix. The ASE extraction from the conventional method was probably able to release the PAHs from the matrix, contrary to the pyrolysis which did not bring enough energy to break the PAH-matrix bonds, explaining underestimation of the PAH concentrations with Py-GC-MS/FID.

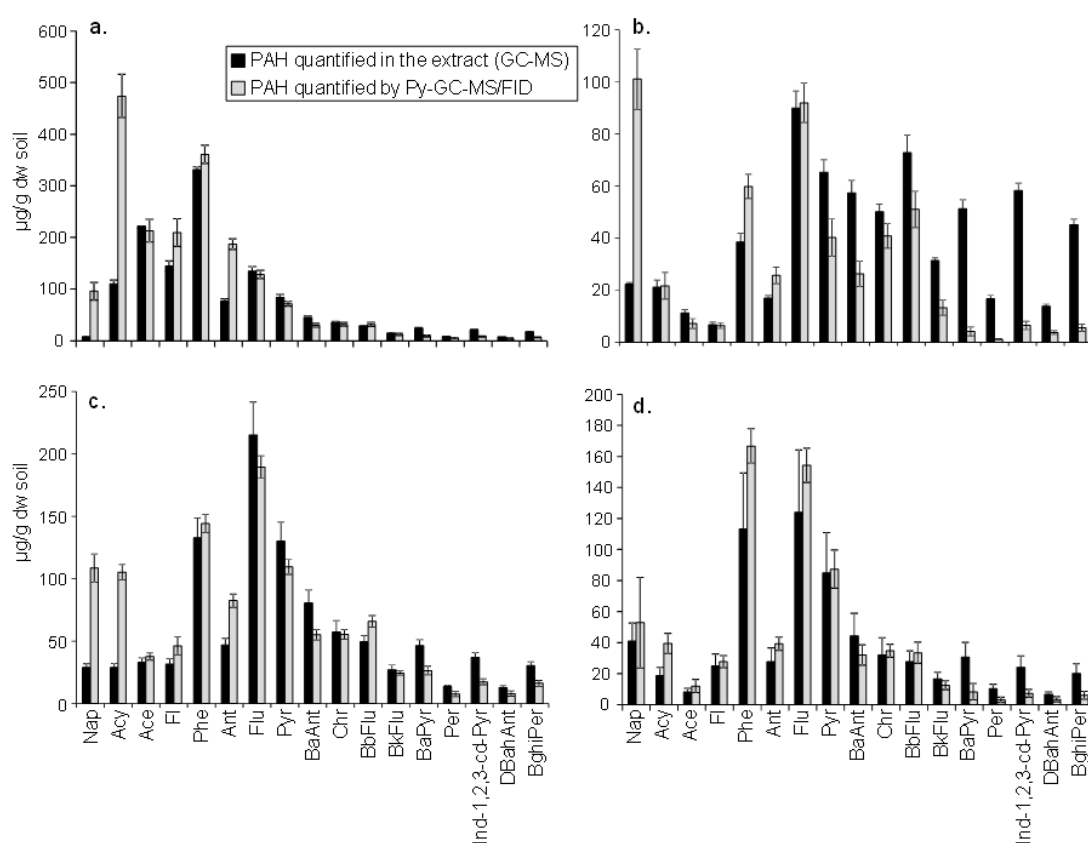
For all the collected samples, except for the Umeå wood-treating facility soil, the standard deviations obtained with the Py-based method were relatively high compared to those acquired with the conventional quantification method. This was not the case for the CRM sample. This sample exhibited very good match in PAH concentrations between both methods except, as mentioned above, for naphthalene and acenaphthylene (Fig. 3a). The comparison of the concentrations obtained with the Py-based and conventional methods with the values from the certificate showed excellent correspondence for both methods (Fig. 3b).



**Figure 3:** Comparison of the PAH concentrations (a) obtained by Py-GC-MS/FID and with the conventional method for certified reference material CRM-BCR 524, and (b) with the values reported on the CRM certificate, \* indicating certified values. PAH abbreviations are reported in Table 1. The error bars represent standard deviation ( $n=3$  for the conventional method and  $n=5$  for the Py-GC-MS/FID method).

The high variability noted for most of the collected soils which was not observed for the CRM can be explained by the higher particle size of samples ( $< 500 \mu\text{m}$ ) compared to the CRM ( $< 62.5 \mu\text{m}$ ) [39].

Additionally, the preparation of the CRM intended to decrease to a minimum the sample heterogeneity as the soil was homogenized in a turbula mixer and subsequently in a jet mill and particles larger than 125  $\mu\text{m}$  were removed [39]. The heterogeneity of the collected sample was probably enhanced by the low sample masses used for the pyrolysis analysis (0.15–3 mg). Therefore we decided to test our method on samples with smaller particle size. Parts of the 500  $\mu\text{m}$  samples were then crushed to pass through a 100  $\mu\text{m}$  sieve and PAH contents were determined by Py-based and conventional methods. As shown in Figs. 4 and 5, grinding the samples to particle size < 100  $\mu\text{m}$  decreased significantly the sample heterogeneity (in comparison with Figs. 1 and 2, respectively).



**Figure 4:** Comparison of the PAH concentrations obtained by Py-GC-MS/FID and with the conventional method for (a) the Homécourt, (b) the Neuves-Maisons, (c) the Moyeuve-Grande coking plant soils and (d) the Rennes gas plant soil crushed < 100  $\mu\text{m}$ . PAH abbreviations are reported in Table 1. The error bars represent standard deviation ( $n=2$  for the conventional method and  $n=5$  for the Py-GC-MS/FID method).

### 3.2. Prospects and limitations of the Py-GC-MS/FID method for PAH quantification

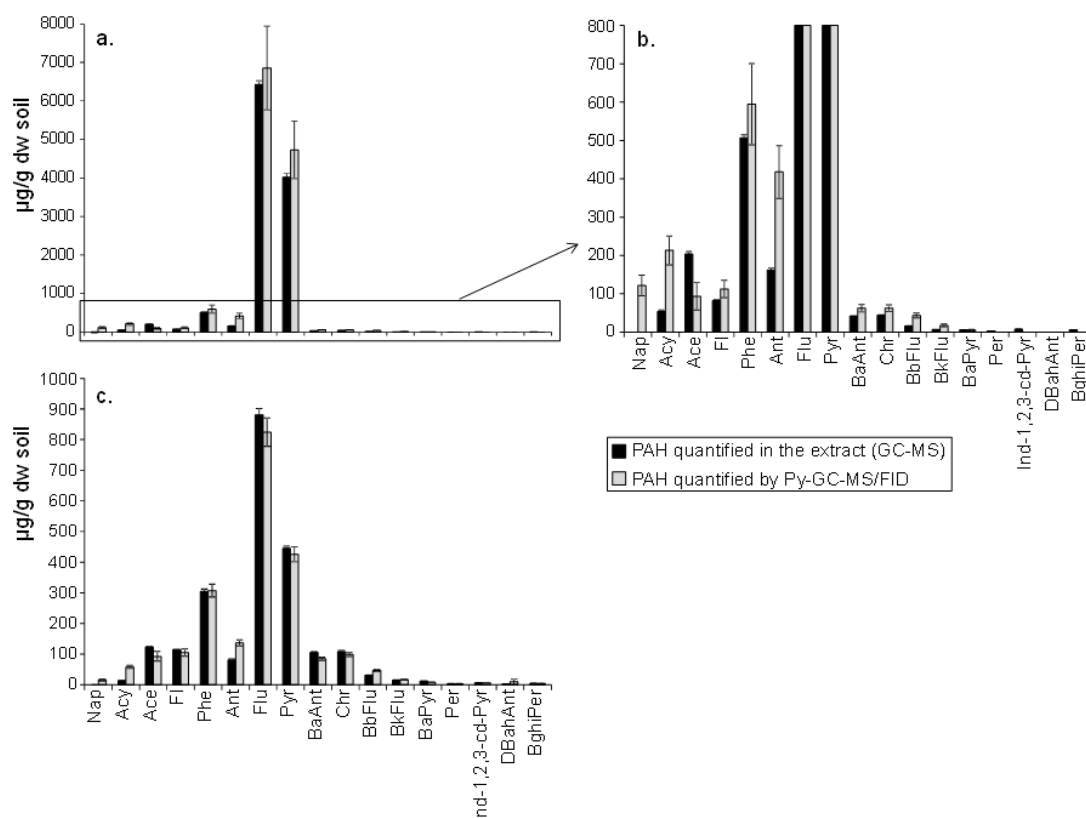
The Py-based method was particularly sensitive to the sample heterogeneity. It is directly linked to the low amount of sample required for the analysis. This issue can be overcome by increasing the sample

homogeneity. The more obvious way seems to be crushing the sample to lower particle size which was proven effective.

The differences in the LMW contents obtained with both methods remains to be explained, even though hypotheses have been stated, as it can lead to an overestimation of the LMW PAHs in the case of the Py- GC-MS/FID or in an underestimation of those compounds in the case of the conventional method. The analyses of spiked samples using both methods might be able to bring some answers and especially to evidence the volatilization of LMW compounds in the case of the conventional method however the thermal breakdown may be harder to identify. The chromatograms of the PAH solution for calibration of the Py-GC-MS/FID did not reveal the presence of smaller units such as toluene and benzene which classically result from the thermal cracking of larger molecules. It is very likely that if a thermal cracking occurred during the pyrolysis of the soil samples they affected macromolecules and kerogen. A solution to check the thermal stability of the soil kerogen at 450 °C would be to analyze a soil previously extracted with solvent by Py-GC-MS/FID and look for the presence of LMW PAH.

Another issue with this method was the underestimation of the PAH concentrations in one sample (from Neuves-Maisons coking plant) likely caused by a strong PAH binding to the matrix. However, determination of PAH concentrations in soil samples are often done for risk assessment and the risk of such contamination is directly linked to its availability, i.e. the strength of the bond between the PAH and the matrix.

Beside the very limited time required for an analysis (5 min of pyrolysis+20 min of GC run) this method present other advantages. Only low amount of sample is necessary which can have multiple implications. It allows analyzing rare or “precious” samples available in very limited amount (rhizospheric soils, samples from microcosm experiment, extraterrestrial samples...). Moreover, the low sample amount, combined with the short-time analysis allow easily carrying out replicate analyses.



**Figure 5:** Comparison of the PAH concentrations obtained by Py-GC-MS/FID and with the conventional method for (a) Midi-Pyrénées wood-treating facility soil, (b) a zoomed portion of the previous graph and (c) the Umeå wood-treating facility soil crushed < 100  $\mu\text{m}$ . PAH abbreviations are reported in Table 1. The error bars represent standard deviation ( $n=2$  for the conventional method and  $n=5$  for the Py-GC-MS/FID method).

#### 4. Conclusion

The Py-GC-MS/FID-based method developed in this study was proven to be effective to quantify PAHs in contaminated soils. Excellent results were obtained for the highly homogeneous CRM whereas important variability was obtained on contaminated samples crushed < 500  $\mu\text{m}$ . This high variability was prevented by crushing the sample to lower particle size (< 100  $\mu\text{m}$ ). Further investigations will be carried out to elucidate the discrepancies of the LMW PAH concentrations between the Py-based and the conventional methods. This fast, economical and eco-friendly method appeared to be a promising tool for PAH quantification in various matrixes, and it has to be tested on a wider variety of samples (sediments, suspended particulate matter...). The samples tested in this study exhibited a wide range of PAH concentrations and distributions but the PAH contents were relatively high and the method needs to be tested on samples presenting lower PAH concentrations. The impact of other parameters

such as the OM content, the aging level, and the presence of other organic compounds and contaminants will also be investigated.

As a link between the PAHs quantified by Py-GC-MS/FID and the level of availability was suspected, this method could then be adapted to other applications such as the determination of PAH availability.

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