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Analysis of polycyclic aromatic hydrocarbons in contaminated soil by Curie point pyrolysis coupled to gas chromatography–mass spectrometry, an alternative to conventional methods

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Abstract

Curie point pyrolysis gas chromatography–mass spectrometry (Py–GC–MS) has been compared with classical extraction procedures (Soxhlet, sonication, KOH digestion, microwave-assisted) followed by GC–MS analysis for the determination of polycyclic aromatic hydrocarbons (PAHs) in contaminated soil. In each case, the efficiency of the technique was examined for 16 PAHs included in the US Environmental Protection Agency Priority Pollutant List. The results indicate that the recovery of PAHs is dependent on the extraction technique. The highest recoveries of PAHs were obtained with Curie point pyrolysis and KOH digestion. Py–GC–MS appeared to be interesting alternative method for the determination of PAHs in contaminated soil. The results were validated by certified soil (CRM 104) analysis.

Keywords: Pyrolysis; Extraction methods; Soil; Environmental analysis; Polynuclear aromatic hydrocarbons

1. Introduction

Among known organic micropollutants (xenobiotics), polycyclic aromatic hydrocarbons (PAHs) are an important group due to their widespread distribution in the environment [1]. The main sources of PAHs are incomplete combustion and diagenetic processes of organic matter, and to a smaller extent in forest fires and more scarcely microbiological synthesis or transformations. Due to their mutagenic and carcinogenic properties [2], concentrations of 16 PAHs, classified as priority pollutants by the US Environmental Protection Agency (EPA) and the European Union, have been investigated in various matrices like sediments, soils, air particulates, petroleum and organisms.

Many analytical techniques have been developed and subsequently applied for the monitoring of these compounds in the environment. Sample preparation and especially extraction is a critical step in organic contaminant analysis because it is time-consuming and in many cases becomes the origin of quantification errors. The preferable extraction technique is usually based on the extraction efficiency, selectivity, its simplicity of operation, smallest amount of solvent used, size of sample, rapidity, the ease of automation, sample throughput and cost.

Curie point pyrolysis (Py) associated with GC–MS is a powerful method for structural analysis of non-volatile compounds, such as synthetic plastics [3], rubbers [4], and paints [5]. Because of its high heating velocity, accurate temperature reproducibility, and wide temperature range, Py–GC–MS has successfully been applied to various compounds and matrices like analysis of soil organic material [6] and polluted sediments [7], analysis of fossil biomaterials [8–10], distinguishing soil humus types [11], and forest and agricultural soil determination [12,13]. These applications led us to test this technique for PAH characterisation in contaminated soil.

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The results of this attempt are reported notably in assessing Py–GC–MS to recover PAHs from contaminated soils. By using a similar analytical scheme, namely extraction, purification, and GC–MS quantification steps, a comparison of Curie point pyrolysis with conventional extraction techniques namely Soxhlet, focused microwave-assisted extraction (MAE), sonication, and KOH digestion [14–17] was made. Evaluation of Curie point pyrolysis technique is based on its recovery efficiency, accuracy, and repeatability.

2. Experimental

2.1. Reference materials and natural matrices

Two types of soil samples were used as analytical references. One belongs from an electrical plant (Rogerville, France) known as heavily contaminated soil by PAHs. It was ground, sieved, homogenised, and freeze-dried for further treatment. The second one is a Certified Reference Material (CRM 104-100, R.T. Corporation, Wyoming, USA) certified by EPA SW846 (3rd ed.) Methods 3530C (Soxhlet extraction) and 8270C (semivolatile organics by GC–MS) [18,19].

2.2. Standards, solvents, and reagents

The 16 studied PAHs range from two- to six-ring aromatic compounds. All solvents used were of analytical grade (Riedel-de Haën, Seelze, Germany and SDS, Peypin, France). The perdeuterated PAHs as internal standards were obtained from Cambridge Isotope Labs. (Andover, MD, USA) comprising [$^2H_{10}$]phenanthrene, [$^2H_{10}$]fluoranthene, [$^2H_{10}$]pyrene, [$^2H_{12}$]chrysene, [$^2H_{12}$]benzo[*a*]pyrene, [$^2H_{12}$]benzo[*ghi*]perylene. PAHs used for calibration (SRM 2260 containing 24 aromatic hydrocarbons, in toluene with a nominal concentration of 60 $\mu g\,ml^{-1}$) were obtained from the US National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA [20].

Prior to fractionation, silica gel 60 and alumina (70–230 mesh, Merck, Darmstadt, Germany) were cleaned by overnight Soxhlet extraction using dichloromethane–methanol (1:1, v/v), and then activated and stored at 150 °C.

2.3. Extraction procedures

Blank experiments were carried out along with each applied technique (same analytical procedure without the contaminated soil matrix) and did not show any contamination. Four hundred microlitres of a solution containing the perdeuterated PAHs in dichloromethane (concentration 250 $\mu g\,ml^{-1}$), were added to the matrix prior to the extraction as internal standard.

2.3.1. Soxhlet extraction

Soil subsamples (10 g) were placed into a cellulose extraction thimble (150 mm × 35 mm i.d.), inserted into upper Soxhlet assembly (250 ml) fitted with a 500 ml round-bottom flask. Two successive extractions were performed with 350 ml of dichloromethane for 24 h. The extract was reduced to a small volume (a few millilitres) using a rotary evaporator. The final concentration was done under a gentle nitrogen stream (30 °C).

2.3.2. Sonication extraction

Ten grams of a soil subsample and 50 ml dichloromethane were first mixed with a vortex homogeniser (Top Mix 94323, Bioblock) for 3 min and then extracted in an ultrasonic bath (Prolabo, frequency 40 kHz) for 15 min. Following sonication, the sample was centrifuged at 47000 $m{\cdot}s^{-2}$ for 5 min and then the supernatant was filtered (Whatman Glass Fiber, GFC Filters). Three successive extractions were performed on each sample as described earlier. The combined organic extracts were reduced to a small volume using a rotary evaporator and the final concentration was done under a gentle nitrogen stream.

2.3.3. Microwave-assisted extraction

Ten grams of hydrated soil subsamples (2 ml of water) were placed into the extraction vessels with 40 ml of dichloromethane. Focused microwave-assisted extractions were performed at a 2450 MHz frequency using a Maxidigest 350 apparatus (Prolabo, France) with a programmable heating power of 30 W, during 10 min [21]. The organic phase was filtered and concentrated as described earlier.

2.3.4. Alkaline saponification

Soil subsamples (10 g) were heated under reflux for 3 h in a mixture (300 ml) of 0.5 M KOH in 95% methanol–toluene (2:1, v/v). After cooling to room temperature, the organic phase was separated, the methanolic layer was extracted with 3× 50 ml toluene. Toluene extracts were combined, washed with distilled water, dried with activated sodium sulphate (150 °C overnight) and then filtered and concentrated as described earlier.

2.4. Clean-up of the aromatic fraction (F2)

The glass column (30 cm × 1 cm i.d.) was packed with 8 g of 70–230 mesh silica gel and 8 g of 70–230 mesh alumina (top of the column), both deactivated with 5% of distilled water. An aliquot of the dry extracts (30 mg in 1 ml heptane) was placed on the top of the column and then fractionated into aliphatic hydrocarbons (F_1), aromatic hydrocarbons (F_2) and polar compounds (F_3) using 30 ml *n*-heptane (F_1), 20 ml *n*-heptane–dichloromethane (90:10, v/v), 40 ml *n*-heptane–dichloromethane (80:20, v/v) (F_2) and 40 ml dichloromethane–methanol (95:5, v/v) (F_3), respectively. Aromatic fraction was reduced to few μl in dichloromethane, under gentle nitrogen stream, and analysed by GC–MS.

2.5. Gas chromatography–mass spectrometry conditions

Qualitative and quantitative GC–MS analyses of PAHs were carried out with a Hewlett-Packard 5890 GC system (with an electronic device to regulate the carrier gas pressure) equipped with a DB-5MS column (60 m × 0.25 mm, 0.25 μm) from J&W Scientific (Folsom, CA, USA) and coupled to a Hewlett-Packard 5989A MS Engine mass spectrometer. The spectrometer was operated in the single ion monitoring (SIM) mode using the molecular ion (*m*/*z*) of each compounds at 1.23 scans s^{-1} (naphthalene: 128; acenapthylene: 152; acenaphthene: 154; fluorene: 166; phenanthrene and anthracene: 178; deuterated phenanthrene: 188; fluoranthene and pyrene: 202; deuterated fluoranthene and deuterated pyrene: 212; benzo[*a*]anthracene and chrysene: 228; deuterated chrysene: 240; benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*a*]pyrene: 252; deuterated benzo[*a*]pyrene: 264; dibenzo[*ah*]anthracene: 278; indeno [1,2,3-*cd*]pyrene and benzo[*ghi*]perylene: 276; deuterated benzo[*ghi*]perylene: 288). The transfer line was held at 295 °C and the source at 240 °C. Electron impact mass spectra were acquired at 70 eV. A 1 μl aliquot of the sample was injected using a splitless injector (60 s of equilibrium time). Helium was used as carrier gas and at a constant flow rate of 1 ml min^{-1}. The oven program was started at 30 °C for 1 min, then 50 °C min^{-1} up to 120 °C, and finally 4 °C min^{-1} up to 295 °C and holding it for 15 min. PAHs response factors were measured by injecting a solution of SRM 2260 containing 24 PAHs and spiked with perdeuterated compounds used as internal standards in each sample.

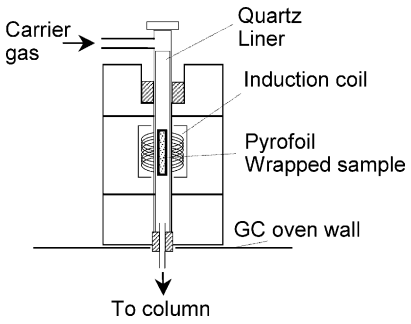

Fig. 1. Schematic of the Curie point pyrolyser.

2.6. Curie point pyrolysis procedure

2.6.1. Instrumentation

A direct thermal desorption of the sample is made by the Curie point pyrolyser. This technique is based on induction heating of a ferromagnetic foil called pyrofoil, placed in an oven equipped with a radio frequency field to reach Curie point temperature (160–1040 °C), a point where pyrofoil loses its magnetic properties and simultaneously characterise the specific property of a heated alloy. Raising time temperature occurs in less than 0.2 s and is highly reproducible. A sample is weighed and wrapped in a pyrofoil, inserted into the sample quartz tube and placed within the centre of coil (Fig. 1). A preheated carrier gas is positioned above the sample tube and the oven is maintained at high temperature to prevent the condensation of pyrolysates into the sample and transfer tubes. The sample is desorbed using the pyrofoil heating and finally the pyrolysates are

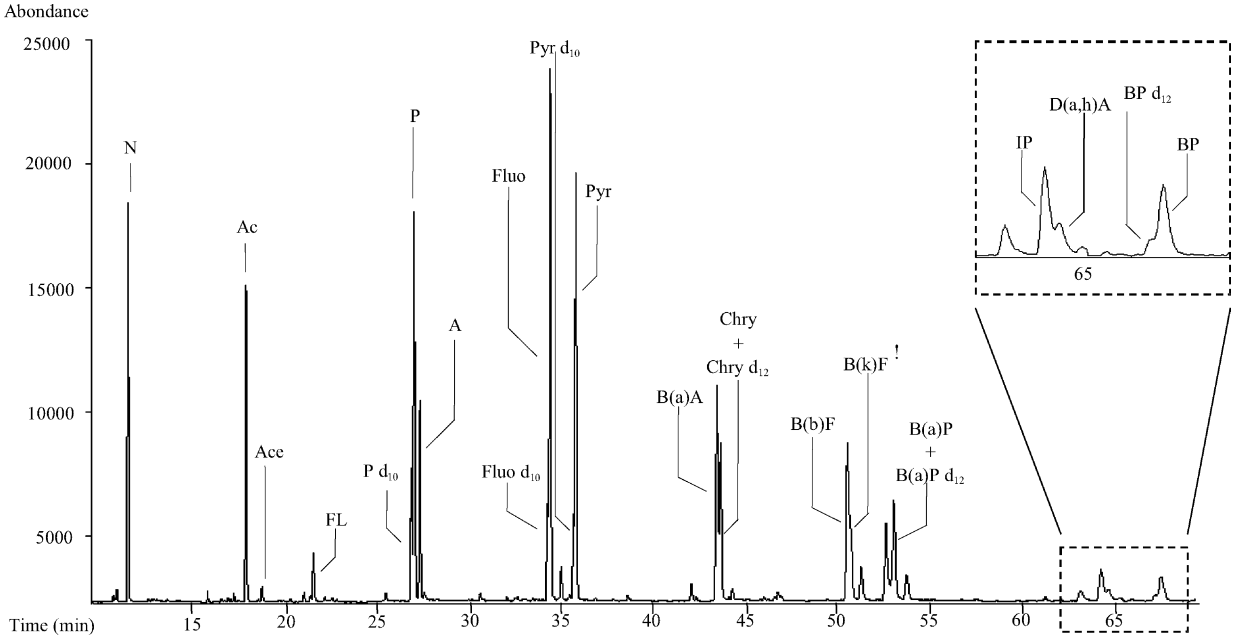

Fig. 2. Py–GC–MS (selected ion monitoring mode) of an sample soil analysis. Note the coelution denoted by an asterisk (N: naphthalene; Ac: acenaphtylene; Ace: acenaphthene; FL: fluorene; P: phenanthrene; A: anthracene; Fluo: fluoranthene; Pyr: pyrene; B[*a*]A: benzo[*a*]anthracene; Chry: chrysene; B[*b*]F: benzo[*b*]fluoranthene; B[*k*]F: benzo[*k*]fluoranthene; B[*a*]P: benzo[*a*]pyrene; IP: indeno[1,2,3-*cd*]pyrene; D[*ah*]A: dibenzo[*ah*]anthracene; BP: benzo[*ghi*]perylene).

transferred to an on line GC column through the needle at oven temperature.

2.6.2. Conditions

The Curie point pyrolyser (JHP-3/3S, Japan Analytical Industry, Tokyo, Japan) is directly coupled to HP 5890 GC (without electronic device to regulate the carrier gas pression) and HP 5988A MS system both from Hewlett-Packard, USA. The conditions are similar to those used above except for the carrier gas (hydrogen). About 30 mg of soil are directly desorbed at 590 °C for 10 s (Pyrofoil OFO-590, Japan Analytical Industry, Tokyo, Japan) and the pyrolyser oven temperature as well as the Py–GC interface are kept at 290 °C.

An example of chromatogram of contaminated soil obtained with Py–GC–MS is given in Fig. 2. A coelution has been noted between structural isomers: benzo[*k*]fluoranthene is not enough separated from benzo[*b*]fluoranthene.

3. Results and discussion

3.1. Comparison of the methods by general parameters

In addition to extraction efficiency, it is interesting to compare the relative merits of each extraction technique. A comparison of general parameters of the different extraction methods is shown in Table 1.

The extraction time for Curie point pyrolysis is very short compared to Soxhlet extraction. A such extraction speed permits the treatment of a high number of samples in a very short time (this is a major advantage for laboratories undertaking routine analysis). The KOH digestion, sonication and MAE time are between those of the two previous techniques. Solvent consumption is an important parameter above all for economical and environmental reasons. From this point of view, the better technique is the direct thermal desorption (no solvent needed).

Reconcentration and clean-up steps have to be performed for all extraction techniques except for Curie point pyrolysis. The contamination risk for those extraction techniques which require reconcentration and clean-up steps are higher than for Curie point pyrolysis.

In order to estimate possible memory effects in the pyrolyser injector chamber, we have done regularly blank experiments between injections. It did not lead to any noticeable contamination. Nevertheless, the difference between pyrolyser and injector temperatures (≈300 °C) does imply more frequent replacement of the injector insert. In the same manner it is inevitable that interferent compounds present in the contaminated soil sample are co-injected into the column. It could result in shortening column life time. The possible coelution of interfering compounds with compounds of interest, probably one of the major drawbacks of this method, may cause some quantification problems even in the SIM mode. Coelution did not occur in the studied samples but it must be checked for other compounds and/or matrices.

Taking into account general criteria like extraction time, solvent consumption and ease of handling, direct thermal desorption seems to be the preferable technique. Nevertheless, with this technique, a data analysis error could result from the small sample size (30 mg). In fact, too small a sample could not be representative of the whole contaminated soil. This very small subsample size is critical. In order to minimise the errors due to the subsample size, the sample preparation is essential. In addition to a meticulous sampling, the whole sample must be grounded finely and accurately with an appropriate crushing device then sieved and finally carefully homogenised. In these conditions, the subsampling errors are reduced.

3.2. Recoveries of PAHs from contaminated soil

The detailed results for each PAH, comparing Curie point pyrolysis and extraction techniques discussed earlier are summarised in Table 2 and represented in Fig. 3.

Each extraction of the contaminated soil from an industrial plant was repeated five times and analysed using GC–MS. In each case, the 16 individual PAHs mentioned earlier were identified and quantified. Six perdeuterated PAHs were used for quantification of the respective PAHs: [$^2H_{10}$]phenanthrene (naphthalene, acenaphtylene, acenaphthene, fluorene, phenanthrene, anthracene); [$^2H_{10}$]fluoranthene (fluoranthene); [$^2H_{10}$]pyrene (pyrene); [$^2H_{12}$]chrysene (benzo[*a*]anthracene, chrysene); [$^2H_{10}$]benzo[*a*]pyrene (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene);

Table 1
Comparison of general parameters for the different extraction techniques

General parameter	Pyrolyser	Soxhlet	Sonication	MAE	Saponification
Sample	30 mg	10 g	10 g	10 g	10 g
Extraction time	10 s	48 h	45 min	10 min	3 h
Solvent consumption	None	700 ml	150 ml	40 ml	360 ml
Reconcentration step	None	Yes	Yes	Yes	Yes
Clean-up	None	Yes	Yes	Yes	Yes
Cost of equipment	High	Low	Low	Medium	Low
Operator skill	Low	Low	Low	Medium	Low
Contamination risks	Low	Medium	Medium	Low	High

MAE: microwave-assisted extraction.

Table 2
Extraction of individual PAHs (mg kg^{-1} dry soil) from contaminated soil: comparison of extraction techniques

Compound	Mean (R.S.D., %)				
	Pyrolysis	Soxhlet	Sonication	MAE	Saponification
Naphthalene	27 (14.2)	0.4 (47.5)	nd	nd	0.2 (36.6)
Acenaphtylene	32 (10.1)	13 (2.2)	11 (6.7)	11 (12.4)	11 (29.1)
Acenaphthene	5 (29.8)	2 (33.5)	1 (27.0)	2 (23.6)	3 (41.4)
Fluorene	10 (24.9)	2 (62.7)	3 (27.0)	5 (12.1)	8 (18.7)
Phenanthrene	70 (19.7)	52 (9.2)	45 (9.3)	58 (15.6)	69 (3.4)
Anthracene	40 (10.6)	26 (5.9)	20 (10.6)	27 (16.6)	34 (7.7)
Fluoranthene	122 (8.5)	131 (2.0)	109 (10.7)	136 (2.4)	140 (2.6)
Pyrene	114 (8.8)	103 (2.0)	85 (8.1)	106 (10.1)	118 (3.8)
Benzo[*a*]anthracene	73 (6.9)	70 (19.1)	66 (8.9)	73 (16.1)	68 (5.3)
Chrysene	72 (3.4)	70 (16.9)	68 (6.6)	81 (6.4)	74 (0.9)
Benzo[*b*]fluoranthene	161 (5.9)	124 (3.4)	113 (8.8)	126 (6.8)	157 (8.5)
Benzo[*k*]fluoranthene	63 (9.4)	42 (9.1)	39 (4.3)	45 (7.1)	64 (9.9)
Benzo[*a*]pyrene	116 (12.6)	95 (6.2)	90 (9.4)	100 (6.5)	124 (6.0)
Indeno[1,2,3-*cd*]pyrene	60 (28.7)	68 (2.0)	64 (7.6)	69 (7.3)	76 (7.8)
Dibenzo[*ah*]anthracene	23 (20.6)	14 (13.8)	15 (9.2)	16 (12.1)	18 (13.3)
Benzo[*ghi*]perylene	69 (17.0)	56 (6.3)	53 (4.1)	57 (9.0)	69 (15.8)
Total	1058 (3.4)	867 (4.4)	794 (6.0)	910 (4.2)	1026 (3.0)

MAE: microwave-assisted extraction (all concentrations are expressed as the mean of five replicates with the relative standard deviation given in parenthesis); nd: not detected.

[$^2H_{12}$]benzo[*ghi*]perylene (dibenzo[*ah*]anthracene, indeno [1,2,3-*cd*]pyrene, benzo[*ghi*]perylene).

Table 2 shows that the alkaline saponification and the direct thermal desorption are more efficient than sonication for the recovery of PAHs in soil (1026, 1058 and 794 mg kg^{-1} respectively), whereas Soxhlet extraction and focused microwave-assisted extraction shows median values (867 and 910 mg kg^{-1}, respectively).

About the repeatability, for the whole PAH contents, the relative standard deviation (R.S.D.) obtained for Curie point pyrolysis is also in the same range as given by alkaline saponification. R.S.D. are lower than 5% in all cases except for sonication which shows a relative standard deviation of 6%. Curie point pyrolysis shows a small R.S.D. (3.4%) involving a good repeatability for this method.

Direct thermal desorption and KOH show good results in comparison to Soxhlet which is hitherto a preferred method used for a long time and considered by many governmental agencies as the reference method for the extraction of PAHs (EPA, Method 3540A) [18].

Saponification has been previously described as a very efficient method in the determination of PAHs in soil [22,23].

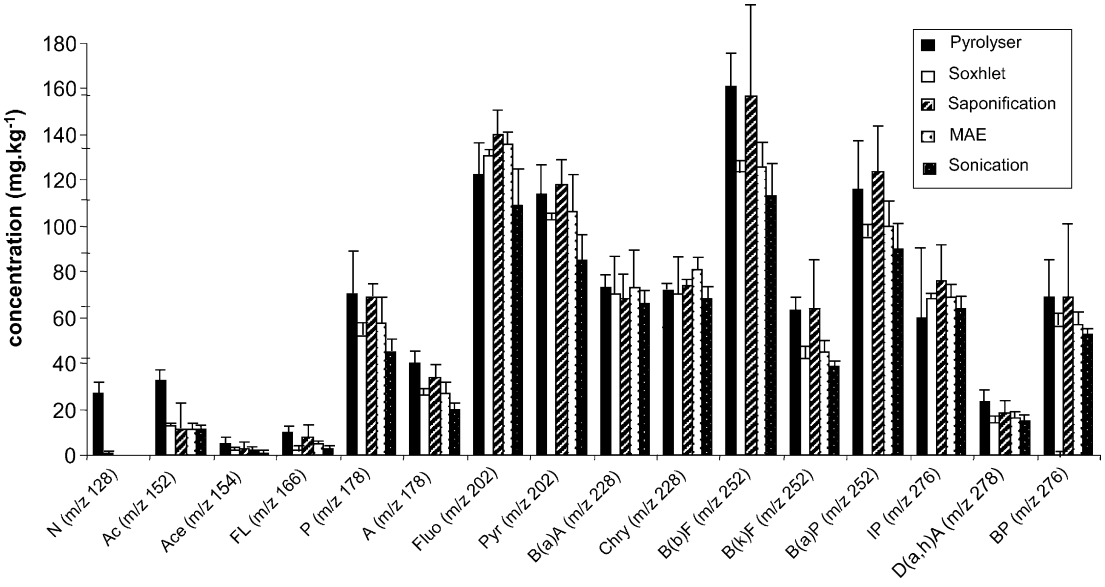

Fig. 3. . Concentration (in mg kg^{-1}) of the studied PAHs obtained by pyrolyser extraction, Soxhlet extraction, sonication, microwave-assisted extraction and saponification.

Table 3
Py–GC–MS LODs and LOQs of PAH compound class

Compound	Limit of detection ($mg\,kg^{-1}$)	Limit of quantification ($mg\,kg^{-1}$)
LMW	0.02–0.4	0.05–0.8
Three- to four-rings	0.2–0.8	0.4–1.7
HMW	0.8–8	1.7–10

LMW: low-molecular-mass; HMW: high-molecular-mass.

This digestion method is known to be able to breakdown polymeric structures of organic compounds like humic acids by cleavage of ester bonds. As a consequence, the accessibility of the solvent to extract the PAHs, which are frequently associated with the organic matrix of the soil, is significantly increased. Unfortunately, this high efficiency is counterbalanced by many steps in the method and impurities in the final extract [17]. For this reason, alkaline digestion required an extensive clean-up before quantification.

Direct thermal desorption gives the same result as KOH and this method is rapid, without clean-up step and other pretreatments.

Concerning individual PAHs, R.S.D. are very different depending on the usual technique. The R.S.D. are more important for some compounds like naphthalene, acenaphthene and fluorene. The amounts of analyte in the tested soil seems to be related to spread of results. Thus, variations generated by the sample treatment step (extraction/concentration) and the extract analysis (detection/integration) appear to be more significant as it is well known for small amounts or traces. Nevertheless, from the point of view of individual R.S.D., the repeatability of the Py–GC–MS is quite close to sonication, is slightly worse than the repeatability of MAE and is better than the other techniques.

3.3. LOD and LOQ

In order to determine the limit of detection (LOD) and the limit of quantification (LOQ) of Py–GC–MS, we used Soxhlet pre-extracted soil (Rogerville, France). After checking for absence of PAHs by another Soxhlet extraction and GC–MS analysis, this "cleaned-soil" was used as a matrix and spiked, directly inside the pyrofoil, with standard PAH solutions, then analysed with Py–GC–MS. The LOD and the LOQ depend on the compound class (Table 3). The LODs and LOQs vary, respectively, between $20\,\mu g{\cdot}kg^{-1}$ and $5\,mg{\cdot}kg^{-1}$ and between $50\,\mu g{\cdot}kg^{-1}$ and $10\,mg{\cdot}kg^{-1}$. These LODs and LOQs are quite high particularly for high-molecular-mass PAHs. The lack of sensitivity for heavy compounds is an important drawback for this method and it means that Py–GC–MS would be rather applicable to the screening for contaminated soils.

3.4. Validation of Py–GC–MS by certified reference material (CRM 104)

Five Py–GC–MS analyses for certified soil (CRM 104) have been performed and the PAHs obtained have been compared to the reference values (Table 4). This CRM represents a weak contaminated soil by low- and high-molecular-mass PAHs. This certified soil is selected in order to determine Py–GC–MS efficiencies for low-molecular-mass PAH analysis.

The concentrations found in CRM 104 using Curie point pyrolysis are in good agreement with the certified concentrations, which were based on Soxhlet extraction [18]. All recoveries are in the confidence intervals. PAHs with high-molecular-mass are detected but are not quantifiable

Table 4
Concentrations (in $mg\,kg^{-1}$ dry weight) of PAHs in CRM 104 determined by EPA methods and Py–GC–MS ($\alpha = 0.025$; n =1–4)

Compounds	Py–GC–MS		EPA Methods	
	Value (R.S.D., %)	Confidence interval	Reference value	Confidence interval
Naphthalene	0.78 (9.9)	0.57–0.99	0.77	0.59–0.94
Acenaphtylene	0.85 (13.5)	0.65–1.05	1.21	0.82–1.59
Acenaphthene	0.72 (17.4)	0.64–0.80	0.77	0.67–0.88
Fluorene	0.73 (14.2)	0.51–1.15	0.65	0.56–0.74
Phenanthrene	6.97 (6.7)	6.50–7.44	5.79	4.93–6.66
Anthracene	1.60 (4.4)	1.13–2.07	1.44	1.15–1.73
Fluoranthene	24.51 (3.8)	22.10–26.92	24.6	19.7–29.4
Pyrene	15.80 (9.7)	11.84–23.76	15.0	11.6–18.5
Benzo[*a*]anthracene	7.59 (8.3)	6.02–9.16	7.98	6.70–9.26
Chrysene	10.42 (7.3)	8.20–12.24	8.60	7.05–10.1
Benzo[*b*]fluoranthene	10.21 (5.4)		9.69	
Benzo[*k*]fluoranthene	nq		5.10	
Benzo[*a*]pyrene	nq		5.09	4.25–5.94
Indeno[1,2,3-*cd*]pyrene	nq		4.46	3.45–5.47
Dibenzo[*ah*]anthracene	nq		1.55	
Benzo[*ghi*]perylene	nq		3.58	2.65–4.51

The reference values were determined by EPA SW846 (3rd ed.) Methods 3540A (Soxhlet extraction) and 8270A (semivolatile organics by GC–MS); nq: not quantified ($<10\,mg\,kg^{-1}$).

because of their low level of occurrence in this certified soil ($<10\,mg\,kg^{-1}$).

Py–GC–MS is efficient for analysis of low-molecular-mass PAHs in weakly contaminated soil, while analysis of high-molecular-mass PAHs at low levels is not suitable under these conditions.

We need to emphasise that the analytical conditions have been chosen in order to compare as much as possible Py–GC–MS with the other techniques. Nevertheless, the high-molecular-mass PAHs quantification can be improved with the following conditions:

(i) a higher temperature (+30 °C) and a "constant flow" mode for the chromatographic injector in order to avoid discrimination between high- and low-molecular-mass PAHs;
(ii) a shorter fused silica capillary column with lower stationary phase film thickness (0.1 μm);
(iii) an electronic device to regulate the carrier gas pressure that could not be respected simultaneously in the both laboratories involving in study.

4. Conclusion

The analyses of a contaminated soil and a certified reference material showed that Curie point pyrolysis is an useful technique for the determination of PAHs from soils as compared to classical methods like Soxhlet, sonication, KOH digestion, and microwave-assisted techniques.

Curie point pyrolysis is particularly effective for low-molecular-mass PAHs; the quantification of high-molecular-mass PAHs is complicated by the specific lack of sensitively of the technique for these compounds. In addition, the small subsample size is critical and involves a meticulous sampling and homogenisation. Concerning the repeatability, this method is in the range of the classical techniques and do not lead to a real improvement. Concerning the main advantages, this method demands a short operating time and is achieved without any extraction solvent. In addition, the validation of the method with a certified soil showed good accuracy for the measured PAHs. In spite of the observed LODs and LOQs, particularly for high-molecular-mass PAHs, the experimental results of this study allow to conclude that Py–GC–MS is an alternative method applicable to screening of contaminated soils or sediment.

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