

Evaluating emission levels of polycyclic aromatic hydrocarbons from organic materials by analytical pyrolysis

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Abstract

A procedure in off-line analytical pyrolysis was investigated for the rapid determination of polycyclic aromatic hydrocarbons (PAHs) evolved from thermal degradation of organic materials. Samples spiked with perdeuterated PAHs were pyrolysed at 1000 °C for 60 s by means of a resistively heated filament pyrolyser inserted into a glass chamber connected to a cartridge with a sorbent (XAD-2 resin). PAHs trapped onto the resin were extracted with dichloromethane and analysed by gas chromatography–mass spectrometry (GC–MS). The analytical performance of the overall procedure (precision, recovery, effect of experimental parameters) was evaluated by pyrolysing a bituminous coal certified reference material (CRM). Emission levels of naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene were determined for bituminous and anthracite coals, tyre, and cellulose. Despite some limitations, the method was adequate to the purpose of quantitatively measuring the tendency of various materials to release volatile PAHs upon heating.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are undesired toxic by-products generated from a variety of human activities related to thermal treatments of coal, wood, oil derivatives and other organic materials [1–3]. In coke manufacturing, for example, coal is heated in the absence of oxygen (pyrolysis) and the process is a significant source of PAHs into the atmosphere [4–7]. Pyrogenic PAHs are also formed during combustion of organic materials and may reach the environment uncombusted. Emission of PAHs associated with combustion include fossil fuel utilisation for residential heating, transportation and power generation, biomass burning and incineration for refuse disposal. Besides operational conditions (oxygen content, temperature and residence time), the chemical nature of the raw

material being heated is crucial for determining the type and quantity of evolved products.

Emission factors (amount of contaminant released per unit material) of PAHs associated to the utilisation of organic materials can be assessed by smoke and stack analyses [8–10], while laboratory experiments with pilot plants and bench-scale reactors enable the determination of emission factors generated under different regimes, including pyrolysis [11–16].

Among analytical techniques, flash pyrolysis (Py) in combination with gas chromatography–mass spectrometry (GC–MS) could be usefully applied to rapidly estimate PAHs evolved from heating organic matter under controlled conditions. Common techniques utilised in combination with GC–MS, include microfurnaces, and inductively (Curie-point) or resistively heated filament pyrolysers. Two different configurations are possible: *on-line*, the GC–MS apparatus is directly interfaced to the pyrolyser; *off-line*, the pyrolyser is disconnected to the GC–MS apparatus, and pyrolysis products are trapped prior to GC–MS analysis.

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On-line Py–GC–MS has been applied to study the nature and relative abundance of PAHs evolved from organic materials [17–19], but studies addressed to absolute quantitation are scant [20]. The ability of Py–GC–MS to quantify PAHs has been demonstrated for environmental matrices [21–23], but the method is essentially a thermal vaporisation of native PAHs from the sample. Moreover, drawbacks caused by mass discrimination and memory effects have been documented for on-line pyrolysis, mainly due to mass transfer through the Py–GC interface [21,24]. Although more time consuming, off-line pyrolysis could be taken into consideration in order to overcome the problems encountered in the on-line configuration.

The aim of this study was to investigate analytical heated filament pyrolysis for the absolute quantitation of PAHs evolved from pyrolysis of organic materials. To this purpose, a procedure was developed using a simple off-line Py apparatus recently adopted in our laboratory for performing pyrolysis with silylating reagents [25,26]. The procedure was tested on a reference material (a bituminous coal) and applied to different organic materials representative of PAH precursors in thermal processes.

2. Experimental

2.1. Samples

The certified reference material (CRM) bituminous coal GBW 11111a issued by the China National Center for Quality Supervision and Test of Coal (CCMRI) was purchased from LabService Analytica (Bologna, Italy). This reference coal was tested for homogeneity by CCMRI and certified for volatile matter (VM, 25.3%, w/w, on a dry basis) along with other properties (e.g. elemental analysis C 74.5%, H 4.5%).

A North American bituminous coal (VM 29.5%), an anthracite (Tower, VM 7.8%), and tyre crumbs (VM 70%) were kindly provided by CPL Industries (Chesterfield, UK). Cellulose (microcrystalline) was purchased from Sigma-Aldrich.

With the exception of the CRM, coal samples were reduced in size and homogenised by a IKA A11 analytical mill.

2.2. Solutions

The following master standard solutions were employed:

- The internal standard mix (for EPA 525) containing acenaphthene-d10 (dACE), phenanthrene-d10 (dPHE) and chrysene-d12 (dCHR) at concentrations of 500 mg l⁻¹ each in acetone purchased from Sigma-Aldrich.
- The PAH-Mix 14 solution containing naphthalene, 1- and 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[ghi]perylene

certified at concentrations of 10 mg l⁻¹ for each species in acetonitrile purchased from Dr. Ehrenstorfer GmbH (Germany) through LabService Analytica (Italy).

- Triphenylmethane (TPM, 1.00 mg l⁻¹) in dichloromethane (DCM) prepared by weighing the pure compound purchased from Sigma-Aldrich.
- Calibration solutions were prepared from the master standard solutions by proper dilutions with DCM (the solvent used in the analytical procedure).

2.3. Pyrolytic equipment

The apparatus employed for off-line pyrolysis experiments has been described in a previous paper [25]. It consisted of a glass tube (pyrolysis chamber) designed for the probe of a CDS 1000 pyroprobe equipped with a resistive heated platinum filament (see Fig. 1). The exit was connected through a Tygon[®] tube to a cartridge for air monitoring containing a XAD-2 resin as adsorbent (orbo-43[®] purchased from Supelco).

2.4. Standard procedure

The analytical procedure is schematically summarised in Fig. 1. A weighed amount of sample (in the 10–13 mg range) was introduced into the quartz tube, and held by quartz wool at the middle part of the tube. The sample was evenly spread with 6 × 10⁻³ ml of the master standard solution of deuterated PAHs (3 × 10⁻³ mg absolute quantity for each dPAH). The probe was inserted into the pyrolysis chamber fitted with the cartridge containing the XAD-2 resin. The apparatus was fluxed with a nitrogen stream at 200 ml min⁻¹ for a few seconds, then the sample was pyrolysed at 1000 °C (set temperature) for 60 s at the maximum heating rate (20 °C ms⁻¹). After pyrolysis, the chamber with the connected cartridge (including the Tygon tubing) was eluted with 5 ml DCM, then 0.100 ml TPM solution (50 mg l⁻¹) were added to the solution which was stored at -15 °C prior to GC–MS analysis.

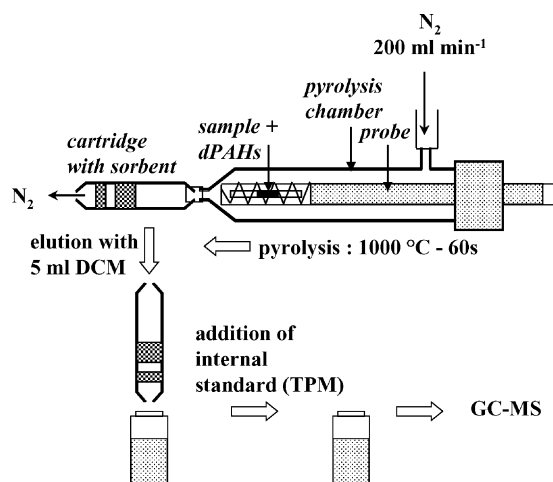


Fig. 1. Scheme of the apparatus utilised for off-line pyrolysis experiments with the illustration of the principal steps of the analytical procedure.

Preconcentration of DCM solutions was not performed, as solvent evaporation with a nitrogen stream resulted in a significant loss of naphthalene.

2.5. GC–MS analysis

Sample solutions (1 μ l) were injected under splitless conditions into a 1078 Varian injector port maintained at 280 °C of a Varian 3400 gas chromatograph connected to a Varian Saturn 2000 mass spectrometer. Analytes were separated by a MDN-5S (Supelco) fused-silica capillary column (stationary phase poly(5% diphenyl/95% dimethylsiloxane), 30 m \times 0.25 mm, 0.25 μ m film thickness) with the following temperature program: from 50 °C (held for 2 min) to 300 °C at 10 °C min⁻¹, using helium as carrier gas (at constant pressure, 33 cm s⁻¹ linear velocity at 200 °C). Mass spectra were recorded under electron impact (70 eV) at a frequency of 1 scan s⁻¹ over a m/z range of 45–450.

2.6. Quantitation

PAHs selected for quantitation are listed in Table 1. The quantity Qh (mg) of each PAH evolved from pyrolysis of W grams of sample is expressed as EL (emission level):

$$EL \text{ (mg g}^{-1}\text{)} = \frac{Qh}{W}$$

Qh was calculated from the chromatographic peak area Ah of the evolved PAH and the peak area Ad of perdeuterated PAH (dPAH) using the equation:

$$Qh = \frac{Qd Ah}{Fh Ad}$$

where Qd was the quantity of dPAH added to the coal sample (3×10^{-3} mg). The peak areas Ah and Ad were determined from mass chromatograms using the ions reported in Table 1. Fh was the response factor for the quantified PAH species relative to the proper dPAH. Relative response

factors for naphthalene, acenaphthylene, acenaphthene and fluorene were determined with respect to perdeuterated acenaphthene; Fh relative to perdeuterated phenanthrene were utilised for phenanthrene, anthracene, fluoranthene and pyrene. Fh values were back calculated from the equation reported above by analysis of calibration solutions.

2.7. Recoveries

The percentage quantity P of dPAHs recovered at the end of the procedure was calculated from the quantity Qt (5×10^{-3} mg) of TPM added to the final solution using the following equation:

$$P = \frac{Qt Ad 100}{Fd At Qd}$$

where At was the peak area of triphenylmethane (TPM) determined at m/z 244, and Fd was the relative response factor of dPAH with respect to TPM determined from the analysis of calibration solutions.

The value of P calculated for the overall procedure described in Section 2.4 represents the procedural recovery R (Table 2). Breakthrough tests were performed by connecting a second cartridge to the first one (in turn inserted into the pyrolytic chamber) and eluting the second cartridge with 5 ml DCM. Elution efficiency was determined by eluting the first cartridge consecutively with two separate fractions of 5 ml DCM (first and second fraction). Finally, the quantity of dPAHs deposited onto the probe was determined by thoroughly washing the probe and the filament with DCM to a final volume of 5 ml. Each solution consisting of 5 ml DCM was spiked with TPM as previously described and analysed by GC–MS. The values of P relative to the second cartridge, the second DCM fraction of the first cartridge and the probe, are indicated as L and represent PAH losses due to breakthrough, incomplete elution and condensation, respectively (Table 2).

Table 1

Compounds considered in this study and the corresponding ions selected for quantitation by GC–MS

N	Compound	Ion (m/z)	LOQ (mg g ⁻¹)	R ² (LOQ \div 2.5 mg g ⁻¹)
1	Naphthalene	128	0.002	0.998
2	2-Methylnaphthalene	141 + 142	0.005	0.998
3	1-Methylnaphthalene	141 + 142	0.005	0.999
4	Acenaphthylene	152	0.002	0.998
5	Acenaphthene-d10	162	–	–
6	Acenaphthene	153	0.003	0.999
7	Fluorene	165	0.006	0.999
8	Phenanthrene-d10	188	–	–
9	Phenanthrene	178	0.002	0.999
10	Anthracene	178	0.003	0.999
11	TRIPHENYLMETHANE	244	–	–
12	Fluoranthene	202	0.002	0.998
13	Pyrene	202	0.002	0.996
14	Chrysene-d12	240	–	–

LOQ: limit of quantitation referred to 10 mg pyrolysed sample; R²: correlation coefficient for the linear calibration model in the LOQ \div 2.5 mg g⁻¹ interval. Compound numbers correspond to peak labels in Figs. 2 and 3.

Table 2

Procedural recoveries (*R*) and losses (*L*) of perdeuterated PAHs (acenaphthene-d10: dACE; phenanthrene-d10: dPHE; chrysene-d12: dCHR) from off-line pyrolysis experiments in the absence and in the presence of CRM coal

		dACE (mean \pm S.D.)	dPHE (mean \pm S.D.)	dCHR (mean \pm S.D.)
Without coal				
<i>R</i>	1° cartridge (first fraction)	87 \pm 6 (<i>n</i> = 2)	86 \pm 6 (<i>n</i> = 2)	67 \pm 2 (<i>n</i> = 2)
<i>L</i>	2° cartridge	2 \pm 1 (<i>n</i> = 2)	2 \pm 1 (<i>n</i> = 2)	4 \pm 1 (<i>n</i> = 2)
<i>L</i>	1° cartridge (second fraction)	n.d.	n.d.	n.d.
<i>L</i>	Probe	n.d.	n.d.	n.d.
With CRM coal				
<i>R</i>	1° cartridge (first fraction)	52 \pm 3 (<i>n</i> = 6)	54 \pm 10 (<i>n</i> = 6)	37 \pm 14 (<i>n</i> = 6)
<i>L</i>	2° cartridge	6.7 \pm 0.1 (<i>n</i> = 3)	9.2 \pm 0.2 (<i>n</i> = 3)	5.1 \pm 2.3 (<i>n</i> = 3)
<i>L</i>	1° cartridge (second fraction)	7.6 \pm 2.6 (<i>n</i> = 6)	2.9 \pm 1.3 (<i>n</i> = 6)	0.7 \pm 0.5 (<i>n</i> = 6)
<i>L</i>	Probe	3.6 \pm 2.5 (<i>n</i> = 6)	2.9 \pm 2.4 (<i>n</i> = 6)	6.5 \pm 6.0 (<i>n</i> = 6)

n.d.: not detected (*S/N* < 3); S.D.: standard deviation.

2.8. Blank tests, linear dynamic range, limit of quantitation

Calibration solutions containing decreasing concentrations of PAHs (starting from 5 mg l⁻¹) at constant concentrations of internal standards were analysed by GC–MS to the end of establishing linear regression fit and limit of quantitation (LOQ, as that concentration giving signal to noise ratio *S/N* ~10). Typical results are reported in Table 1 and are calculated for 10 mg of pyrolysed sample. A calibration solution at 1 mg l⁻¹ level was routinely analysed along with sample solutions.

Procedural blank tests, accomplished by using the procedure described in Section 2.4 in the absence of sample, resulted in no significant contamination (*S/N* < 3).

3. Results and discussion

3.1. Off-line pyrolysis of organic materials: qualitative aspects

The standard off-line pyrolysis procedure investigated in this study is schematically summarised in Fig. 1. The sample spiked with surrogate PAHs (perdeuterated, dPAHs) is pyrolysed at 1000 °C, the evolved products are trapped in a sorbent, de-sorbed with dichloromethane and analysed by GC–MS. The GC–MS traces obtained by applying this procedure to a suite of organic materials representative of possible sources of pyrogenic PAHs are reported in Fig. 2. Fig. 2a shows the chromatogram produced from the analysis of a bituminous coal which is issued as certified reference material (briefly named as CRM-coal). Pyrolysis products identified in the chromatogram include alkylphenols, alkylbenzenes, alkyl-naphthalenes and the corresponding non-alkylated species. Similar chromatograms were obtained from a bituminous coal of different origin (North American, chromatogram not shown). Pyrolysates produced from anthracite display chromatograms with weak signals, in accordance to the lower volatility of low rank coals (Fig. 2b). The chromatogram (Fig. 2c) resulting from the

pyrolysis of tyre crumbs is characterised by an intense peak attributed to limonene and aromatic hydrocarbons derived from the thermal degradation of polyisoprene and styrene–butadiene rubbers. Cellulose, a major constituent of vegetal biomass, produces anhydroglucoses and furans as principal pyrolysis products (Fig. 2d). The presence of levoglucosan, which starts forming at temperatures significantly lower than 1000 °C, indicates that thermal vaporisation of primary pyrolysis products is an important process.

All the investigated materials generate PAHs under the experimental conditions adopted in this study. Chromatographic peaks corresponding to evolved PAHs and perdeuterated PAHs (dPAHs) added to the sample are evidenced in Fig. 3, showing mass chromatograms on selected ions of their mass spectra. Chromatographic peaks corresponding to PAHs with molecular weight (MW) ranging from that of naphthalene (128 Da) to that of pyrene (202 Da) are clearly observed, whereas peaks corresponding to heavier PAHs (MW > 202 Da) are negligible or absent, as illustrated in the inset of Fig. 3 for CRM-coal. High MW PAHs are known to be produced from pyrolysis of coal and other organic materials [12–15], but probably at levels not detectable by our procedure, partly because of the small sample size (<13 mg) subjected to analysis. For this reason, heavier PAHs are not quantified and the discussion will be limited to volatile PAHs, namely those listed in Table 1.

3.2. PAH emission levels from CRM-coal: analytical performance of the procedure

The analytical performance of the procedure was investigated in detail by employing the CRM-coal as test material. Coal is largely applied as a feedstock material and fuel in thermal processes responsible for PAH emission into the atmosphere (e.g. coke production, power generation, residential heating), thus it is a good representative as a PAH producing material. Moreover, the CRM-coal is certified for homogeneity and is commercially available making it possible comparisons between results obtained from different techniques and/or laboratories.

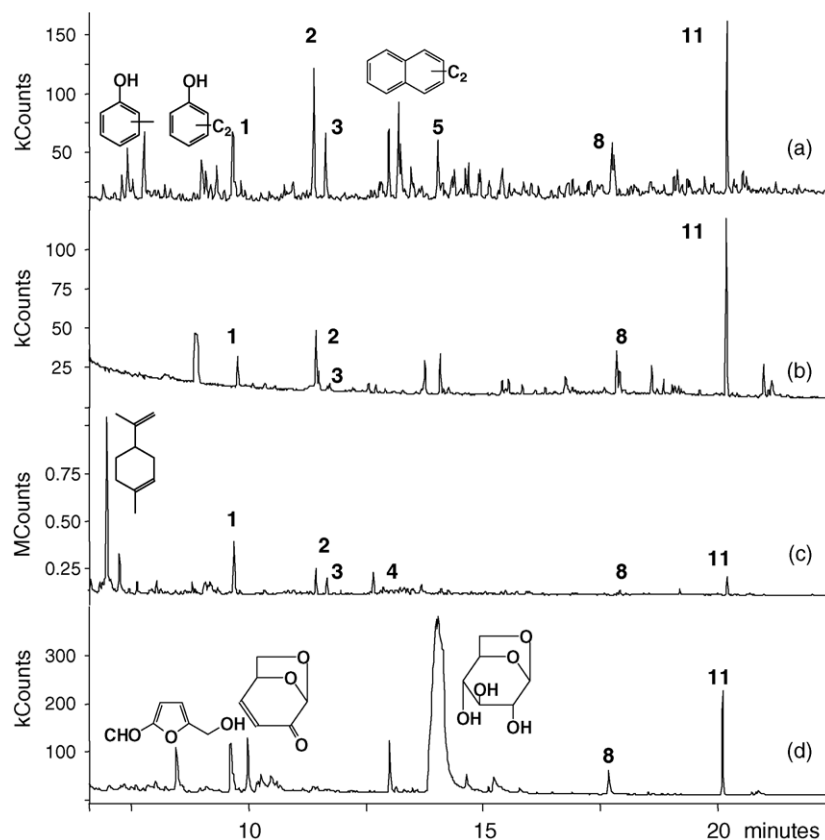


Fig. 2. Total ion chromatograms of pyrolysates obtained from off-line pyrolysis of different organic materials; (a) bituminous coal (CRM), (b) anthracite, (c) tyre crumbs, (d) cellulose. Numbered peaks correspond to the compounds listed in Table 1.

Mean emission levels (ELs) of PAHs determined for CRM-coal using the off-line Py procedure proposed in this study are reported in Table 3 along with the corresponding mass percentage distribution. ELs fall in the 0.03–0.9 mg g⁻¹ range, with the highest values observed for naphthalene and methylnaphthalenes and the lowest for acenaphthene, anthracene, fluoranthene and pyrene. Overall, about 90% of emitted PAHs is accounted for naphthalenes, phenanthrene and fluorene.

3.2.1. Precision

Data dispersion, expressed as percentage standard deviation (RSD), is reported in Table 3 for analyses replicated within a short time period (repeatability) as well as those performed during a long time period (reproducibility). A typical data set exemplified in Table 3 for repeatability, shows that RSD values range from 7.5% (1-methylnaphthalene) to 18% (acenaphthene). This precision is rather satisfactory considering the intrinsic heterogeneous nature of coal and the low sample size (10 mg) subjected to analysis.

As expected, uncertainty associated to analyses performed over a long time period, during which the probe, pyrolysis chamber and operators have been changed, are much higher, with R.S.D. values larger than 17%. Notably, the highest variability (85%) is observed for acenaphthylene.

Precision associated to percentage mass distribution of PAHs measured over a long time period is fairly good for the most abundant species (naphthalenes, fluorene, phenanthrene), displaying R.S.D. values $\leq 15\%$. Among the less abundant PAHs, again acenaphthylene exhibits the largest variability. These variations are tentatively attributed to temperature effects, probably resulting from changes in platinum filament geometry with usage. Therefore, for a reliable comparison between ELs from different materials or conditions, analyses should preferably be performed within a short time period and intervalled with pyrolyses of a standard material (in our case, the CRM-coal).

3.2.2. Recoveries

Procedural recoveries (*R*) and losses (*L*) are determined by the analysis of deuterated PAHs (dPAHs). Data reported in Table 2 refer to a set of replicate analyses performed within a short time period. The values of *R* for pyrolyses accomplished in the absence of coal are around 86% for perdeuterated acenaphthene (dACE) and phenanthrene (dPHE), and 70% for perdeuterated chrysene (dCHR). In the presence of the CRM-coal, *R* values drop to levels around 53% for dACE and dPHE, and to 37% for dCHR. Thus, dCHR was not used as internal standard for calculations.

Three factors that may affect recovery have been investigated: breakthrough, incomplete elution from the

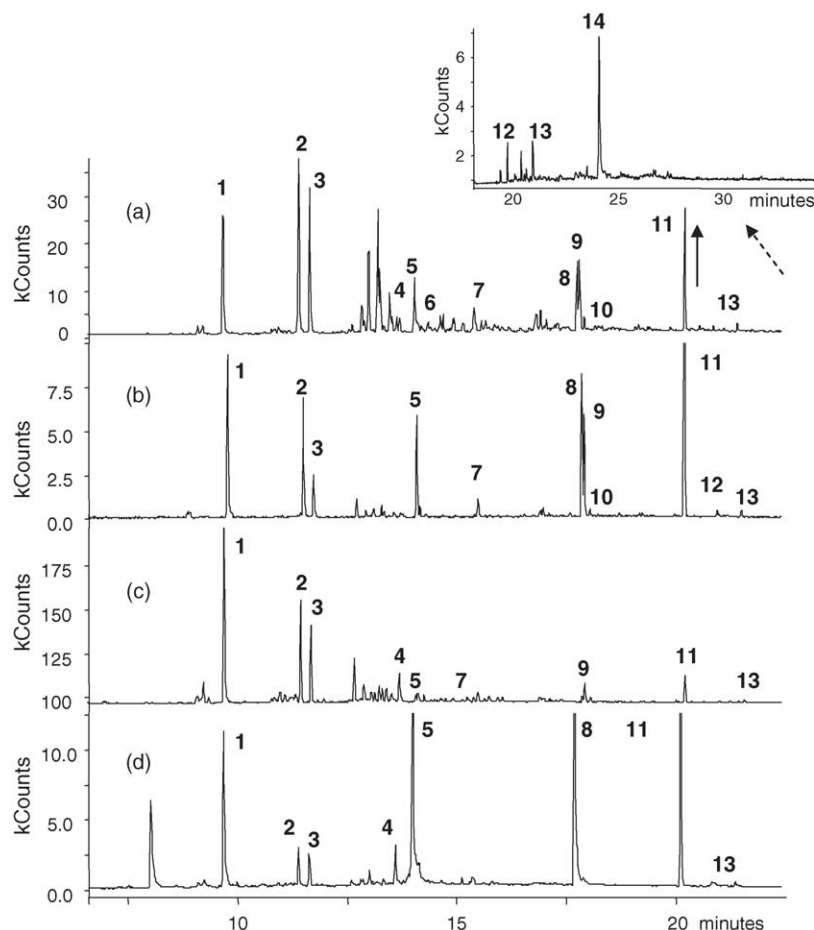


Fig. 3. Mass chromatograms of pyrolysates obtained from off-line pyrolysis of (a) CRM bituminous coal, (b) anthracite, (c) tyre crumbs, and (d) cellulose. Monitored ions (m/z): 128 + 141 + 142 + 152 + 153 + 162 + 165 + 188 + 178 + 202; the inset of Fig. 3 shows the mass chromatogram at m/z 202, 228, 252, 240, 276 and 278 for the elution region of heavier PAHs. Numbered peaks correspond to compounds listed in Table 1.

cartridge and condensation onto the probe. Losses (L) associated to these processes are minimal when pyrolyses are performed in the absence of coal (Table 2).

In the presence of coal, breakthrough increase noticeably (around 7–9%, Table 2), probably due to saturation from pyrolysis products released from the coal. Incomplete elution of PAHs from the adsorbent is responsible for 7, 3

and 0.7% losses for dACE, dPHE and dCHR, respectively. Finally, 3–6% of losses are caused by condensation of PAHs onto the pyrolysis probe. However, data in Table 2 show that a significant percentage of dPAHs lost during the analytical procedure is not accounted for by the investigated factors (breakthrough, incomplete elution, condensation onto the probe). Probably PAHs are trapped onto the carbonised coal

Table 3

Emission levels (EL, mg g^{-1}) and percentage (w/w) distribution of PAHs from off-line pyrolysis of CRM-coal (1000 °C for 60 s)

PAH	EL (a) (mg g^{-1})	R.S.D. (a) (%)	EL (b) (mg g^{-1})	R.S.D. (b) (%)	Distribution (b) (% w/w)	R.S.D. (b)
Naphthalene	0.47	9.3	0.57	37	21.3	9.0
2-Methylnaphthalene	0.87	9.3	0.83	17	33.0	11
1-Methylnaphthalene	0.42	7.5	0.40	17	16.0	9.7
Acenaphthylene	0.044	9.0	0.10	85	3.4	53
Acenaphthene	0.050	18	0.05	31	1.9	34
Fluorene	0.14	12	0.18	42	6.7	15
Phenanthrene	0.27	12	0.29	29	11.4	7.0
Anthracene	0.060	9.4	0.07	45	2.7	23
Fluoranthene	0.028	13	0.04	56	1.5	26
Pyrene	0.044	9.3	0.05	34	2.0	17
Total PAHs	2.40	8.5	2.58	27	–	–

Mean values and percentage relative standard deviations (R.S.D.) relative to: (a) $n = 6$ replicates within a short period (5 days), and (b) $n = 31$ replicates over a long time period (8 months).

network remaining in the quartz tube after pyrolysis, or are thermally degraded. This finding is in accordance to literature data indicating that only a small fraction of deuterated PAHs initially added to a bituminous coal subjected to pyrolysis could be recovered [13].

3.2.3. Effect of experimental parameters

Results from off-line pyrolysis experiments with and without the addition of dPAH, indicate that spiking the coal with the standard solution does not influence the emission levels (ELs) of PAHs. In fact, total ELs (quantified by means of the internal standard triphenylmethane, TPM) are $2.4 \pm 0.5 \text{ mg g}^{-1}$ ($n = 4$, mean \pm S.D.) and $2.5 \pm 0.8 \text{ mg g}^{-1}$ ($n = 6$) for CRM-coal pyrolysed with and without the addition of dPAHs, respectively. Moreover, the precision is better when ELs are calculated with respect to dPAHs (R.S.D. from 4% for fluorene to 25% for acenaphthene, 14% on average, $n = 4$) rather than to TPM (from 18% for naphthalene to 55% for acenaphthene, 31% on average).

The effect of sample size, nitrogen flow rate, pyrolysis time and temperature on the ELs of PAHs are reported in Fig. 4. Reducing the pyrolysis time from 60 to 10 s significantly decreases the quantity of released PAHs. Reduced yields are also observed as a consequence of decreasing flow rate, while the amount of the pyrolysed sample does not influence significantly the analytical results. Overall, small variations of these parameters (time, weight, flow) around the established values are not likely to affect the accuracy of the off-line procedure. Pyrolysis temperature

is a critical parameter, as ELs decrease noticeably with decreasing pyrolysis temperature to 800°C (Fig. 4).

3.3. PAH emission levels of coal, tyre and cellulose

Mean emission level (EL) of PAHs from different organic materials determined by the off-line pyrolysis procedure are reported in Fig. 5. Besides coals with different rank and origin (chinese CRM-coal, North American bituminous coal, and anthracite), analysed materials also included tyre crumbs, and cellulose. All these materials are possible source of PAHs in processes such as coke production (bituminous coal), open burning (biomass), thermal processing of refuse (tyre wastes). The chromatograms of the corresponding pyrolysates have been illustrated in Section 3.1.

ELs for individual PAH species fall within the linear interval established by calibration solutions (Table 1, the only exception is tyre-derived naphthalene), indicating that the method is adequate for measuring EL of organic materials with different propensity to release PAHs. Total ELs range from $0.40 \pm 0.13 \text{ mg g}^{-1}$ ($n = 6$) for cellulose to $9.0 \pm 0.5 \text{ mg g}^{-1}$ for tyre ($n = 3$). The amount of PAHs evolved from the two bituminous coals is similar, with total EL of 2.0 ± 0.1 ($n = 3$) and $2.4 \pm 0.1 \text{ mg g}^{-1}$ ($n = 6$) for North American and Chinese-CRM coals, respectively. Anthracite exhibits total EL smaller than bituminous coals ($0.52 \pm 0.05 \text{ mg g}^{-1}$, $n = 3$) in accordance to the lower volatile matter and rank.

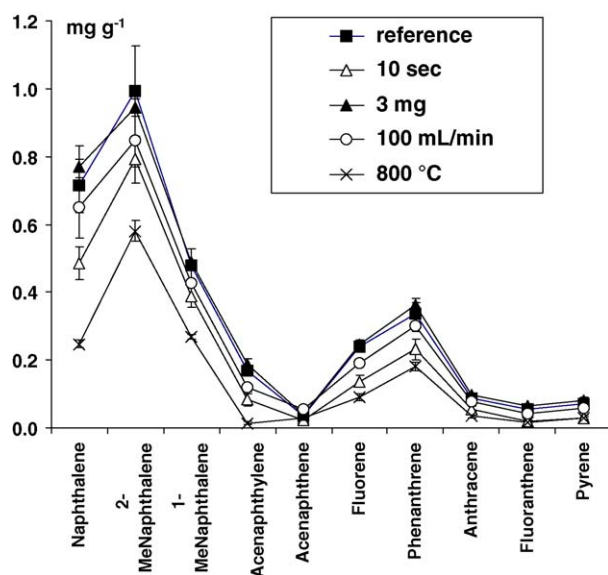


Fig. 4. Effect of experimental parameters on the emission levels of PAHs (mg g^{-1}) from off-line pyrolysis of CRM bituminous coal. Mean values and standard deviations obtained from three replicate pyrolyses. The following conditions were changed with respect to those established for the standard (reference) procedure, while keeping constant the others: pyrolysis time, 10 s (instead of 60 s); sample amount, 3 mg (instead of 10 mg); nitrogen flow rate, 100 ml min^{-1} (instead of 200 ml min^{-1}); pyrolysis temperature, 800°C (instead of 1000°C).

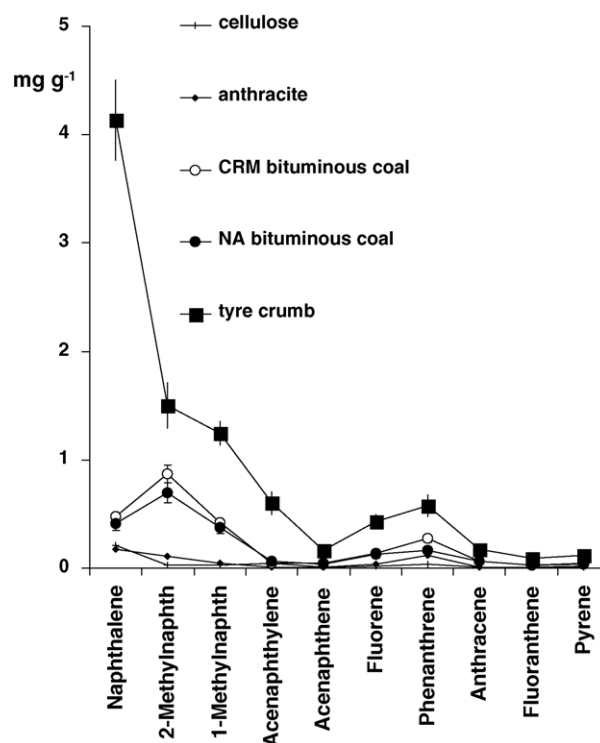


Fig. 5. Emission levels (mg g^{-1}) of individual PAHs from off-line pyrolysis of different organic materials. Mean values and standard deviations from three replicate pyrolyses.

Table 4

Relative distribution (% w/w) of PAHs evolved from off-line pyrolysis of different organic materials (1000 °C for 60 s)

PAH	Cellulose	Anthracite coal	Bituminous CRM	Bituminous coal	Tyre crumb
Naphthalene	53	33	20	20	46
2-Methylnaphthalene	8.1	21	36	35	17
1-Methylnaphthalene	6.6	8.4	17	19	14
2-Ring PAHs	68	62	73	74	76
Acenaphthylene	12	1.0	1.8	3.4	6.7
Acenaphthene	2.0	0.9	2.1	1.7	1.9
Fluorene	4.0	6.6	5.8	6.3	4.8
Phenanthrene	8.3	23	11	8.3	6.4
Anthracene	2.0	1.7	2.5	3.2	1.9
3-Ring PAHs	28	33	24	23	22
Fluoranthene	1.8	2.1	1.2	1.4	1.0
Pyrene	2.3	2.8	1.8	1.9	1.3
4-Ring PAHs	4.1	4.9	3.0	3.3	2.3

Corresponding PAH yields are depicted in Fig. 5.

Fig. 5 and Table 4 show that the distribution of non-alkylated PAHs is featured by naphthalene as the predominant species for all the investigated materials, followed by phenanthrene, acenaphthylene and fluorene. Bituminous coals are characterised by the highest abundance of methylated naphthalenes in the pyrolysates. For all the samples, the molecular distribution is dominated by 2-ring PAHs with 62–76% relative abundance (Table 4), followed by 3-ring PAHs (22–33%), whereas 4-ring PAHs represent 2–5% of total PAHs.

3.4. Comparison with literature

A direct comparison with procedures employing analytical pyrolysers is not possible as published data pertinent to this study are lacking. Thus, the following discussion refers to pyrolysis experiments performed with techniques other than analytical pyrolysis (e.g. reactors, pilot plants, furnaces).

From the values tabulated by Atal et al. [13], total emission factors of 8.4 and 13 mg g⁻¹ for the nine PAH species listed in Table 1 are calculated for a high volatile bituminous coal (volatile matter, VM 34%) and ground tire (VM 52%), respectively. These values include both gaseous and particulate PAH species evolved from pyrolysing the sample at 1150 °C with a residence time of 0.75 s. From the results reported by Mitra et al. [12], total emission factors of 5.5 and 0.38 mg g⁻¹ are obtained for PAHs released from the pyrolysis (at about 980 °C, 0.30 s) of a high volatile bituminous coal (VM 37%) and anthracite (VM 3.3%), respectively. The yield of PAHs evolved from pyrolysis of tyre waste in a pilot plant was 2.8 mg g⁻¹ (for six PAHs at 650 °C) according to Conesa et al. [16]. Finally, the amount of PAHs released from the pyrolysis of cellulose can vary from about 0.1 mg g⁻¹ (600 °C, 6 PAHs) [27] to 2 mg g⁻¹ (8 PAHs, 850 °C) [15]. For comparison, the concentration of PAHs in pyrolysis oil from biomass (wastewood) was 0.02 mg g⁻¹ (5 PAHs, 550 °C) [28].

From this short survey, it appears that the emission levels determined by our procedure (9, 3, 0.5, and 0.4 mg g⁻¹ for tyre, bituminous coal, anthracite and cellulose, respectively)

can be considered fairly consistent with the range of values reported in the literature.

As far as the molecular distribution of PAHs is concerned, there are some common features between our data (see Table 4) and published results on PAH emission. Pyrolysis experiments with reactors generally show that high molecular PAHs (MW > 202 Da) are evolved at much lower levels than more volatile PAHs (MW ≤ 202 Da, two to four rings), and among the latter naphthalene is generally the most abundant non-alkylated species followed by phenanthrene and fluorene [12,13,15,28]. This picture seems to be in accordance to field studies on atmospheric emissions showing that volatile PAHs (MW ≤ 202 Da) are responsible for more than 99%, and 85% of the total (20) PAHs measured in air samples impacted by coke plants, and wood combustion, respectively [7]. Similar studies on coke plants indicated that volatile PAHs, with naphthalene as the most abundant, are predominantly found in the vapor phase, whereas PAHs with MW > 202 Da are associated with particles [5,6]. Although high MW PAHs, such as benzo[a]pyrene, are the principal target in air monitoring studies for their carcinogenic potential, the role of volatile PAHs to air quality and human health is not to be neglected, as gas-phase reactions may transform PAHs into more toxic compounds with direct-acting mutagenicity, such as nitro-PAHs. For instance, it has been shown that nitronaphthalenes and methyl-nitronaphthalenes can contribute significantly to the total mutagenicity of vapor-phase ambient air [29].

The most striking difference in the PAH profiles concerns acenaphthylene and the ratio of alkylated to parent naphthalenes. The yield of acenaphthylene is small in our study compared to other PAHs, but it is reported to be a major PAH in pyrolysates of various organic materials [12,13,16]. At this regards, it is worth pointing out that acenaphthylene is the compound exhibiting the largest variability in our experiments. Under the conditions adopted in this study, 2-methylnaphthalene is the principal PAH found in the pyrolysates of bituminous coal (Table 4), whereas other studies with reactors have reported methyl-naphthalenes at lower yields than naphthalene [12,13].

These differences are not surprising as the formation of PAHs is dependent on several factors, such as pyrolysis temperature and residence time. In particular, the relative abundance of acenaphthylene and alkylated PAHs is strongly affected by pyrolysis temperature [18].

4. Conclusions

A detailed performance study was conducted on the suitability of analytical pyrolysis for absolute quantitation of PAH emission levels from various materials. From the obtained results the following advantages and shortcomings can be evidenced:

The commercially available pyrolyser unit for on-line Py-GC-MS can be easily and conveniently adapted to the off-line configuration proposed in this study (ca. 70 Euros the cost of the glass pyrolysis chamber). The procedure is rapid and simple, so that up to 10 samples could be run in a single day.

The repeatability, limit of quantitation and linearity are reasonably good for properly evaluating the quantity of PAHs emitted from different kinds of materials. The procedure exhibits fairly good reproducibility as far as the mass percentage distribution of evolved PAH species is concerned. However, a certain variability is observed when emission levels are measured over long time periods.

The overall recovery is not quantitative, especially for higher MW PAHs, so that addition of surrogate PAHs as internal standard is performed prior to pyrolysis. Spiking the sample with the standard solution does not affect the pyrolytic behaviour of the material being pyrolysed.

Emission levels determined with the proposed procedure refers to volatile PAHs ($MW \leq 202$ Da) which are known to partition in the gaseous phase in the atmosphere. Larger PAHs ($MW \geq 252$ Da) are not detected probably for the relatively small sample size, and the tendency of less volatile PAHs to be trapped onto the char.

Despite the above mentioned limitations, this study shows that analytical pyrolysis can be profitably used to rapidly discriminate on a quantitative base the propensity of different materials to release PAHs upon heating.

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