



Quantification of polycyclic aromatic hydrocarbons (PAHs) found in gas and particle phases from pyrolytic processes using gas chromatography–mass spectrometry (GC–MS)

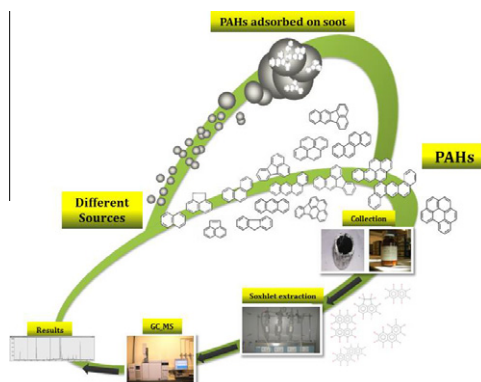
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HIGHLIGHTS

- ▶ A methodology for PAH quantification from thermochemical processes was developed.
- ▶ Quantification of both PAH adsorbed on soot and at the gas phase was considered.
- ▶ The method gives reliable results of PAH from complex samples like soot.

GRAPHICAL ABSTRACT



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ABSTRACT

The outlet stream from combustion processes is a complex mixture of compounds which depends on the specific operating conditions. Thermochemical processes operating under rich fuel conditions enhance the formation of polycyclic aromatic hydrocarbons (PAHs) and soot. PAH play an important role in soot formation, but they can appear adsorbed on soot surface as well as at the gas phase due to their different volatility and molecular weight. Both PAH (the gas phase and adsorbed PAH) fractions are important when considering the total characterization from pyrolytic processes, mainly for determining the emission levels of 16 Environmental Protection Agency (EPA) priority PAH. In this way, an optimized method capable to determine the aromatic compounds in the gas and particle phases in combustion exhaust gases is needed. The method here presented allows the collection and quantification of both the PAH adsorbed on soot and present at the gas phase of the exhaust gases of thermochemical processes. It involves PAH characterization by combining classical Soxhlet extraction of the sample collected, followed by an extract concentration using a rotary evaporator and subsequent micro-concentration under gentle nitrogen stream before the analysis. The EPA-PAH were determined using a gas chromatograph–mass spectrometer (GC–MS). Validation tests using a fully characterized soot, the NIST (National Institute of Standards and Technology) reference material SRM 1650b, and repeatability using diesel surrogate commercial soot named Printex-U, were done. Additionally, experiments of acetylene pyrolysis were carried out and their products analyzed for determining the PAH amount. The results showed good method

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reliability for the determination of 16 EPA-PAH found in the outlet gases, as well as good recovery for the most of PAH and good prediction for the real samples analyzed.

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1. Introduction

Formation of soot in the regions of combustors with locally fuel rich areas is accompanied by the formation of polycyclic aromatic hydrocarbons (PAHs), which can be considered as soot precursors via the hydrogen abstraction-acetylene addition (HACA) mechanism [1–3]. Soot particles from combustion processes are known to be associated to highly carcinogenic and mutagenic compounds such as PAH, which are present at the gas exhaust, but can also appear adsorbed on the surface of soot [4–6]. In some occasions this PAH fraction present on soot particles may be high, with concentration levels of the same order of magnitude or even higher compared to those classically found at the gas phase from pyrolysis or combustion processes.

The Agency for Toxic Substances and Disease Registry (ATSDR) has classified 17 PAH as of greatest concern with regard to potential exposure and adverse health effects on humans [7]. The eight PAH mentioned as known carcinogens by European Union, in the annex VI of the regulation European Commission (EC) 1272/2008 [8], are also included within ATSDR-PAH. The USA Environmental Protection Agency (EPA) completed another list with 16 priority compounds, known as 16 EPA-PAH based on potential toxicity for human exposure or frequency of occurrence at hazardous waste sites. These compounds are: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene. This list is often considered as a reference in environmental sample evaluation [9,10], being some of them important aromatic intermediates in the HACA mechanism during the large PAH and soot formation [2,11,12].

There are in the literature a number of works developed for quantification of PAH using different analytical methods. The quantification of PAH present in the atmosphere is usually made by a combination of ultrasonic extraction and gas chromatography with mass spectrometry (GC–MS) [e.g. 13], and PAH determination in combustion systems mainly rely on techniques such as laser diagnostic, used to study the PAH-soot distribution and for their characterization [e.g. 14,15], mainly in flames. Ballesteros et al. [16] developed a method for determining the 16 EPA-PAH associated to particulate matter from gas exhaust of real engines. Other determinations of PAH have been carried out in fluidized bed combustion by using fluorescence spectroscopy (FS) after ultrasonic extraction with dimethylformamide (DMF) [17–20], and a combination of Soxhlet extraction with gas chromatography–mass spectrometry (GC–MS) was used by Aracil et al. [21] and Font et al. [22] for testing the PAH at the gas phase from polyvinyl chloride and polyethylene pyrolysis, respectively. Other pyrolysates at the gas phase, including PAH, have been determined by the Wornat group [23], by means of GC–MS to obtain kinetic parameters on PAH formation relevant to combustion of solid fuels. Other works using GC–MS, HPLC with ultraviolet–visible diode-array detection for the determination of larger PAH, have been developed by them throughout this decade and with different purposes but under not sooting conditions [24–26]. However, little or none research has been devoted to evaluate the amount of PAH linked on both particulate matter like soot and at the outlet gas stream.

In this context, the present work aims to determine the PAH concentration found at the exhaust gas of thermochemical pro-

cesses, considering both at the gas phase and those PAH adsorbed on the soot. For this purpose, we have adapted and optimized a methodology for the 16 EPA-PAH characterization that can be easily applied to gas exhaust from any thermochemical process, and includes collection of soot and PAH from the gas phase, sample preparation, and analytical procedure.

The method uses a combination of the traditional Soxhlet extraction, concentration of the extract and GC–MS. The analytical method has been optimized for the analysis of PAH formed under pyrolysis processes of gaseous hydrocarbons, such as acetylene and ethylene, using a wide range of well-controlled laboratory conditions. In this respect, it represents an useful complement to the outcomes of experimental works developed in the last years in our research group [27–30].

An appropriate validation of the method and repeatability trials are given here, by using a NIST standard reference material (SRM 1650b) (Table S1 in Supplementary data) and a commercial soot used as diesel surrogate (Printex-U). It is worthwhile to mention that, to our knowledge, not concentration data on PAH of Printex-U are available in the literature.

In addition, the method was verified by sampling and analysis of samples formed from acetylene pyrolysis in a tubular quartz reactor using the same reaction temperature (1223 K) and by varying the inlet fuel concentration between 10,000 ppmv and 30,000 ppmv. As reported previously [31], reaction temperature of 1223 K favoured the PAH formation under similar conditions. The lighter PAH at the gas phase were retained when they passed through a fine tube with XAD-2 resin, whereas the PAH adsorbed on soot were collected by means of a quartz fiber filter. More details on experimental system are shown elsewhere [27,28].

2. Experimental

2.1. Reagents and materials

Sample collection is a very important step in the PAH characterization from pyrolytic processes. The soot and its aromatic compounds associated, formed during the pyrolysis experiments of acetylene, were swept out by the outlet gas stream, and then retained in a quartz fiber filter (30 mm diameter, 100 mm length, pore diameter lower than 1 μ m).

Several researchers have found that semivolatile compounds can be collected on filters such as cellulose acetate, nylon or polytetrafluoroethylene (PTFE) [e.g. 17–20], but when compounds are present at high concentration they can be lost with the outlet gas stream. Adsorbents such as Tenax-GC, XAD-2 resin and polyurethane foam (PUF) [32] have demonstrated efficiency for PAH collection [33]. In general XAD-2 resin presents more efficiency for PAH adsorption and retention than PUF, and shows higher recovery of compounds of two and three aromatic rings like naphthalene, frequently appearing in high amounts at the outlet of combustion processes [34,35]. For these reasons, an XAD-2 resin, supplied by Supelco, has been selected for this study. It was packaged in a thin-tube (300 mm length, 80 mm internal diameter), which was placed immediately after the filter used for soot collection.

A PAH standard mixture (PAH-Mix 63, Dr. Ehrenstorfer-Shäfers) containing the 16 EPA-PAH was used for calibration purposes. It includes: naphthalene 99.8% purity [CAS 91-20-3], acenaphthylene 98% [208-96-8], acenaphthene 99.5% [83-32-9], fluorene 98% [86-73-7], phenanthrene 99.5% [85-01-8], anthracene 99.5%

Table 1
Internal standard used for calibrating of each EPA-PAH.

Internal standard	Polycyclic aromatic hydrocarbons
Naphthalene-d ₈	Naphthalene
Acenaphthene-d ₁₀	Acenaphthylene Acenaphthene Fluorene
Phenanthrene-d ₁₀	Phenanthrene Anthracene Fluoranthene
Chrysene-d ₁₂	Pyrene Benzo(a)anthracene Chrysene
Perylene-d ₁₂	Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenz(a,h)anthracene Benzo(g,h,i)perylene

[120-12-7], fluoranthene 99% [206-44-0], pyrene 99.5% [129-00-0], benzo(a)anthracene 99% [56-55-3], chrysene 99% [218-01-9], benzo(b)fluoranthene 99% [205-99-2], benzo(k)fluoranthene 99% [207-08-9], benzo(a)pyrene 99% [50-32-8], dibenz(a,h)anthracene 99% [53-70-3], indeno(1,2,3-cd)pyrene 99% [193-39-5] and benzo(g,h,i)perylene 99.5% [191-24-2], everyone with concentration of 1000 mg L⁻¹. A deuterated internal standard mixture recommended by EPA method TO-13A [33] (Mix 26, Dr. Ehrenstorfer-Shäfers), of 4000 mg L⁻¹ was also used and included acenaphthene-d₁₀ 99% [CAS 15067-26-2], chrysene-d₁₂ 98.5% [1719-03-5], naphthalene-d₈ 99.5% [1146-65-2], perylene-d₁₂ 99.5% [1520-96-3] and phenanthrene-d₁₀ 99% [1517-22-2]. The internal standard for each target compound is shown in Table 1. For further validation of the method, the standard reference material SRM 1650b for diesel particulate matter, provided by the National Institute of Standards and Technology (NIST) [36], was used.

The solvent used during the Soxhlet extraction and in the calibration was dichloromethane (DCM) 99.5% [CAS 75-09-2] (HPLC grade), supplied by Panreac. The Soxhlet apparatus has a volume of 125 mL and flasks of 250 mL. The size of cellulose extraction cartridge (Filter-lab), placed inside of Soxhlet thimble, was 33 × 94 mm in internal diameter and length, respectively. Printex-U, provided by Evonik Industries, which was used in repeatability test, is a commercial soot considered as diesel soot surrogate, it has been already characterized in previous works [37,38]. Sodium sulfate anhydrous [CAS 231-820-9] (Sigma-Aldrich) was used to eliminate sample moisture during the extraction.

The Helium used as carrier gas in the GC–MS and nitrogen (Air Liquid), as well as the acetylene (Praxair) are of high quality.

2.2. Instrumentation

The GC–MS system consisted of a 7890A gas chromatograph with a 7683B autosampler coupled to a MSD 5975C mass selective

detector from Agilent technologies. The capillary column was a DB-17 ms, 60 m × 0.25 mm ID × 0.25 µm film thickness also supplied by Agilent.

The analytical balance (model GR-120) was supplied by A&D Company, limited. A bank of four heating mantles, supplied by Selecta, was used to evaporate the solvent in the Soxhlet extraction. Extract concentration was achieved by means of a Büchi rotary evaporator.

3. Method proposal

3.1. Overview of the analysis method

Fig. 1 shows the method diagram used for PAH quantification that combines sample Soxhlet extraction, subsequent concentration of the extract by rotary evaporator using an adaptation of the 3540C EPA method [39], followed by GC–MS analysis. Each step will be explained further below.

3.2. Sampling of PAH during pyrolysis processes

The analytical method was developed with the main objective of characterizing the 16 EPA-PAH formed during pyrolysis processes under well-controlled conditions, such as reaction temperature, pressure, gas concentration and gas residence time, which are the typical relevant variables inside combustion chambers.

The reaction temperature was fixed at 1223 K at atmospheric pressure. Experiments were run for 1.5 h, using an acetylene–nitrogen mixture and varying the acetylene concentration from 10,000 ppmv to 30,000 ppmv. Acetylene was chosen because it is believed to be the link between the linear hydrocarbons generated under pyrolysis conditions from fuels and the formation of the aromatic compounds which subsequently lead to soot generation [11].

In this context, the PAH sampling was carried out in different ways. The lightest PAH, which due to their high vapor pressure do not appear condensed and remain in the gas phase, were retained by passing through a narrow tube containing XAD-2 resin. The heaviest PAH, which presumably appear adsorbed on soot, were collected by means of the quartz fiber filter.

3.3. Sample pre-treatment

The EPA methods 8270D and TO-13A, for determination of semivolatile organic compounds and toxic organic air pollutants respectively, were taken as reference with slight modifications, to develop the analytical method presented here. Soxhlet extraction was used as extraction procedure, since the EPA method 3540C [39] mentions that it guarantees good contact between solid sample and solvent.

Prior to Soxhlet extraction, each sample was placed in a cellulose cartridge, whose packaging consisted of quartz wool on the bottom, followed by 3 g of sodium sulfate anhydrous to eliminate sample moisture. Subsequently, and separated by quartz wool,

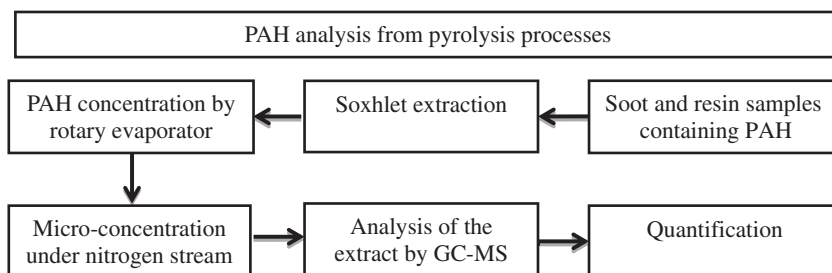


Fig. 1. Procedure of the sample analysis developed to determine PAH concentration.

the target sample with 10 μL of the solution of the five internal standards (Table 1) was added. Then, the cartridge was covered with quartz wool to prevent sample loss during extraction cycles. Finally, the cartridge as a whole was situated inside the thimble of the Soxhlet extractor. The packaging cellulose cartridge scheme is shown in the Supplementary data (Fig. S1).

Internal standards were used for correcting the possible losses of analytes during sample preparation, since chromatographic signal of both target compound and its internal standard have a similar response. Thus, if for any reason target compounds are lost during sample treatment, a proportional amount of its internal standard is lost as well. This ratio of signals, which is independent of the sampling history, is used to obtain the calibration curves and subsequently the analyte concentration [40].

3.4. Classical Soxhlet extraction

The Soxhlet extraction is based on a standardized method for solid sample extraction. Nowadays, it represents the main method of reference to compare the recovery obtained with other extraction techniques [41,42]. In spite of other methods are recommended by EPA and the Food and Drug Administration (FDA), such as supercritical fluid extraction and accelerated solvent extraction, the classical Soxhlet extraction keeps on being the most common of these methods, with proven good recoveries, under different conditions [43].

The cartridge with the sample is placed in the thimble of the Soxhlet extractor, which is gradually filled with solvent from a distillation flask. The assembly extractor is operated as a batch system, since vapor of solvent moves up to a condenser, and floods the thimble. When the liquid reaches the overflow level, a siphon aspirates the solvent from the thimble-holder and unloads it back into the distillation flask [44]. This process is repeated until the extraction is completed. The extraction time for the optimized method was fixed in 24 h using a total amount of 200 mL of DCM and 4 extraction cycles per hour.

3.5. PAH concentration by rota-evaporation and micro-concentration

Semivolatile compounds may be lost during DCM evaporation process. For this reason, the sample concentration is another critical step during the sample treatment. In this way, DCM offers an advantage since has a boiling point far below of those at which target compounds are evaporated. This allowed a fast solvent evaporation at temperatures low enough to prevent significant losses of analytes.

The sample extracts were reduced to approximately 5 mL by rota-evaporation (bath temperature at around 308 K). Then, they underwent micro-concentration using a gentle nitrogen stream to give a final volume of 1.5 mL. This concentration procedure leads to satisfactory results with small extract volumes. It is worth mentioning that this step depends on the concentration of analyte in the sample.

3.6. Chromatographic analysis

GC–MS was used for PAH separation, identification and quantification. Chromatographic conditions were chosen according to EPA recommendations [33]. They were as follows: carrier gas was He (1 mL min^{−1}). Injection mode was splitless (300 °C, 1 μL). Temperature program started at 80 °C held for 15 min, then raised at 5 °C min^{−1} up to 110 °C and held for 5 min, a second heating rate of 5 °C min^{−1} up to 290 °C held for 35 min and finally a third heating rate of 1.5 °C min^{−1} up to 320 °C held for 5 min. The transfer line temperature was set at 280 °C. All analyses were performed in selected ion monitoring mode (SIM) of the MS in order to

Table 2
Monitoring ion profile.

Compounds	Monitored ions	MS window time (min)
Naphthalene-d ₈	136 –108	31.00–36.00
Naphthalene	128 –129	
Acenaphthylene	152 –153	43.00–47.00
Acenaphthene-d ₁₀	164 –162	
Acenaphthene	154 –153	47.01–56.00
Fluorene	166 –165	
Phenanthrene-d ₁₀	188 –189	
Phenanthrene	178 –179	
Anthracene	178 –179	58.00–63.00
Fluoranthene	202 –203	
Pyrene	202 –203	
Benzo(a)anthracene	228 –226	
Chrysene-d ₁₂	240 –236	67.00–72.00
Chrysene	228 –226	
Benzo(b)fluoranthene	252 –253	81.00–84.00
Benzo(k)fluoranthene	252 –253	
Benzo(a)pyrene	252 –253	88.00–93.00
Perylene-d ₁₂	264 –260	
Indeno(1,2,3-cd)pyrene	276 –277	110.00–114.00
Dibenz(a,h)anthracene	278 –279	
Benzo(g,h,i)perylene	276 –277	116.00–120.00

enhance the selectivity and sensitivity of the method. Table 2 shows the SIM profile programmed in the MS; values in bold refer to ion used for quantification and the MS window times in which each ion was monitored. The PAH in the chromatograms were initially identified by means of their retention times and using the NIST 2.0 mass spectral library, working in SCAN mode. The most of the chromatographic peaks showed good resolution and efficiency, this fact can be verified in Fig. S2 (Supplementary material).

4. Results and discussion

4.1. Determination of analytical method characteristics

The calibration curves for each PAH were plotted calculating the ratio between chromatographic area for each target compound related to the area of its corresponding internal standard (A_s/A_{is}) versus amount in ng of PAH standard used for calibration related to the amount in ng of the specific internal standard (m_s/m_{is}).

By analytical reasons, and taking into account the wide concentration range at which PAH are present in the samples, calibration curves were built using eight concentration levels, each one in triplicate. The linear fitting of resultant calibration curves for each compound shows correlation coefficients (R^2) between 0.986 and 0.999, which are shown in Table 3 along with linear range (20–50,000 $\mu\text{g L}^{-1}$ in all the cases) and the main analytical characteristics. The lowest calibration point, 20 $\mu\text{g L}^{-1}$, is equal or higher than all quantification limits (LOQ), which were found to be as low as 0.31 $\mu\text{g L}^{-1}$. This means that, within the range of analysis, quantitative data can be confidently acquired.

The way for determining the amount of PAH in the target samples is shown in Supplementary material, as well as additional verifications for checking the correct calibration of every PAH curve, as recommended by EPA for toxic organic air pollutants [33]. Thus, different parameters were analyzed, such as the RRF_i (relative response factor of each calibration level) and the relative standard deviation percentage (%RSD) (Table S2), which shows the precision of the calibration results, and relative retention time of each calibration level (RRT_i) of both standard and internal standard of each EPA-PAH analyzed (Table S3). The determination of these parameters is also shown in the Supplementary data together with a brief discussion.

Table 3

Analytical characteristics of the optimized method for EPA-PAH determination.

PAH	Correlation coefficient R^2	Linear calibration range ($\mu\text{g L}^{-1}$)	Detection limit LOD ($\mu\text{g L}^{-1}$)	Quantification limit LOQ ($\mu\text{g L}^{-1}$)
Naphthalene	0.997	20–50,000	0.09	0.31
Acenaphthylene	0.990	20–50,000	0.71	2.36
Acenaphthene	0.999	20–50,000	0.53	1.78
Fluorene	0.997	20–50,000	1.62	5.41
Phenanthrene	0.999	20–50,000	0.73	2.44
Anthracene	0.995	20–50,000	1.21	4.04
Fluoranthene	0.998	20–50,000	0.84	2.80
Pyrene	0.998	20–50,000	0.80	2.68
Benzo(a)anthracene	0.994	20–50,000	2.29	7.63
Chrysene	0.999	20–50,000	1.57	5.25
Benzo(b)fluoranthene	0.994	20–50,000	3.30	10.99
Benzo(k)fluoranthene	0.991	20–50,000	3.70	12.35
Benzo(a)pyrene	0.994	20–50,000	5.88	19.61
Indeno(1,2,3-cd)pyrene	0.986	20–50,000	6.00	20.00
Dibenz(a,h)anthracene	0.987	20–50,000	5.83	19.42
Benzo(g,h,i)perylene	0.987	20–50,000	6.32	20.05

4.2. Quality verification of chromatographic and sample treatment processes

The quality control is a fundamental component in the development of any analytical work as the presented in this paper. It guarantees that the study is developed under the quality parameters, which can be monitored at any time, being able to detect when a process has a bad operation, thus being a very useful diagnosis tool to find the possible source of errors [40].

In the present work, several procedures, such as repeatability trials, were carried out for checking the validity of the methodology developed for PAH determination, to both solid and gas phases from combustion processes.

4.3. Repeatability of the sample treatment and chromatographic method

Repeatability is the variability of the measurements obtained by one person, in the same laboratory and using the same devices [40]. In order to verify both the chromatographic method and the sample treatment repeatability, the PAH present in 1.5 g of the carbon black Printex-U were evaluated, with a week of difference between determinations (in total three weeks, with every sample carried out in duplicate). The chromatographic analyses were run immediately after the sample treatment to minimize possible compound losses.

Table 4 and Fig. 2 show the averaged mass fraction of the 16 EPA-PAH for all the trials made, together with the relative standard deviation (RSD) and the results of mass fraction for the three weeks, respectively. In both cases, mass fraction refers to amount in nanograms of PAH per milligram of Printex-U analyzed. The precision of the results expressed as RSD were between 2% and 22% in the most of cases, showing overall a good repeatability. This fact can be confirmed by means of the comparison of the results for each trial in Fig. 2. Since RSD is a value of relative deviation, the compounds with lower mass fraction logically exhibit higher deviations.

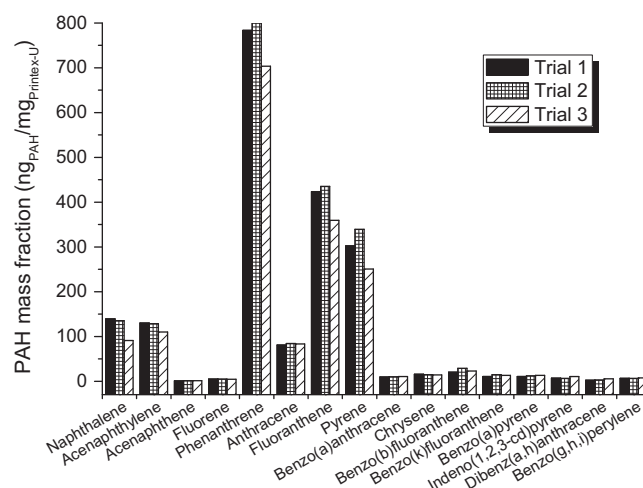
4.4. Validation with a standard reference material

Once the method has been completely defined, its capacity to give acceptable values using known samples was evaluated. Thus, the NIST SRM 1650b, which has been used in different works for evaluating the analytical methods for PAH determination [16,42], was chosen. In this way, the good behavior of the method is evidenced.

Table 4

Averaged mass fraction of PAH from Printex-U and relative standard deviation (RSD) for the results.

Compound	Average ($n = 3$) ($\text{ng}_{\text{PAH}}/\text{mg}_{\text{Printex-U}}$)	RSD (%)
Naphthalene	121.7	22.0
Acenaphthylene	122.8	9.2
Acenaphthene	1.1	17.4
Fluorene	4.8	6.3
Phenanthrene	769.2	7.8
Anthracene	82.9	2.0
Fluoranthene	406.0	10.0
Pyrene	297.5	15.0
Benzo(a)anthracene	10.0	3.0
Chrysene	14.7	4.1
Benzo(b)fluoranthene	24.2	18.6
Benzo(k)fluoranthene	12.8	16.4
Benzo(a)pyrene	11.8	12.7
Indeno(1,2,3-cd)pyrene	8.2	28.2
Dibenz(a,h)anthracene	3.5	45.7
Benzo(g,h,i)perylene	6.6	10.6

**Fig. 2.** Repeatability results of Printex-U, trials for 3 weeks.

The corresponding certified and reference values of PAH reported by NIST are expressed in mass fraction and they are shown in the Supplementary data (Table S1). Four 45 mg aliquots of SRM 1650b were analyzed using the developed method. Table 5 shows

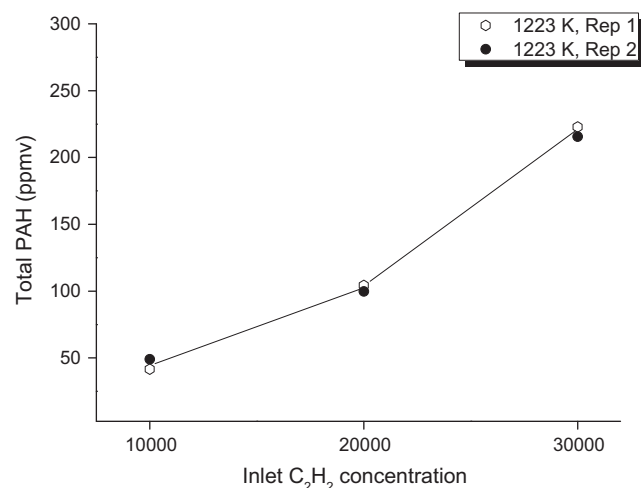
Table 5

Determined values in mass fraction and recovery percentage for SRM 1650b.

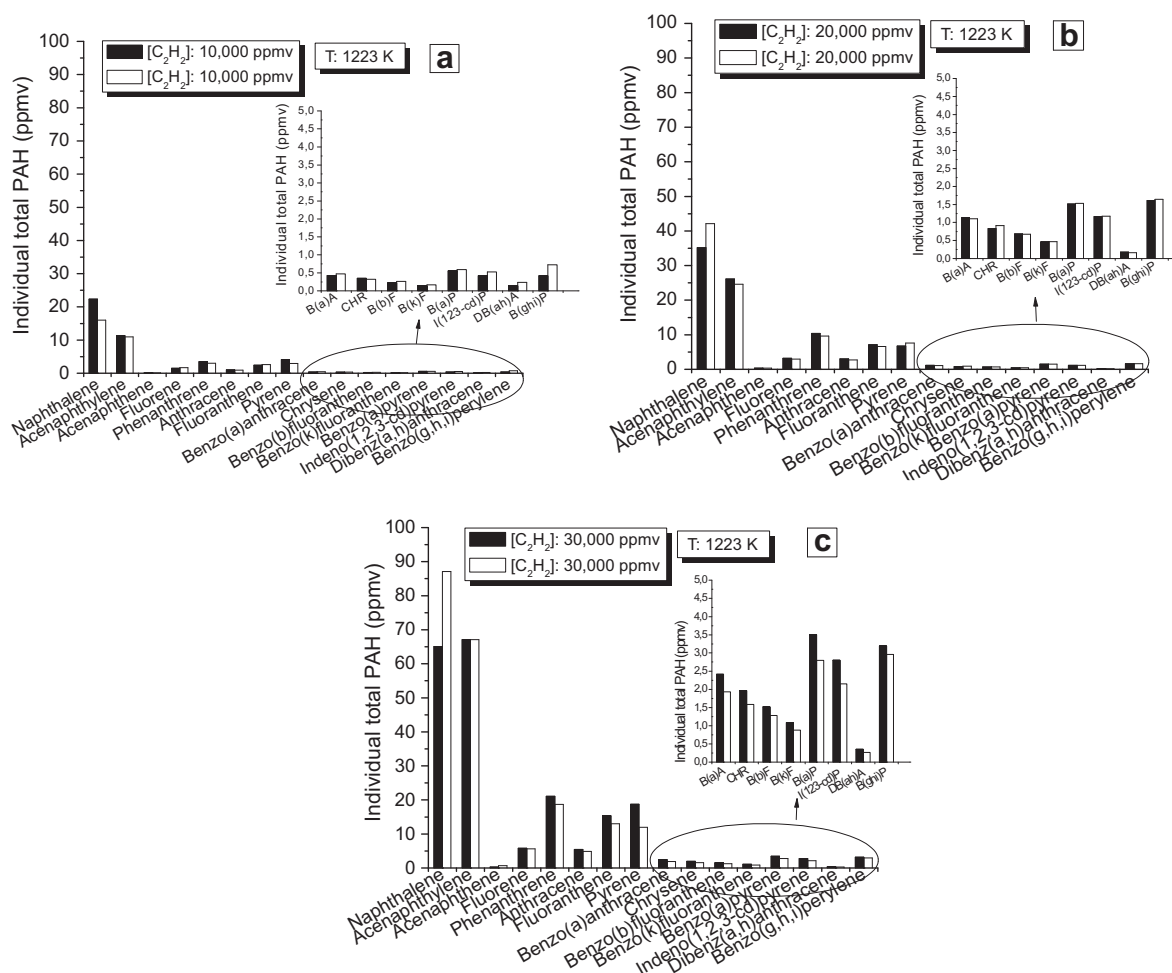
Compound	Average values (ng _{PAH} /mg _{SRM 1650b})	Recovery (%)
Naphthalene	3.27	64
Acenaphthylene	1.19	86
Acenaphthene	0.22	98
Fluorene	1.25	99
Phenanthrene	57.20	82
Anthracene	17.60	229
Fluoranthene	59.33	125
Pyrene	50.82	117
Benzo(a)anthracene	9.62	156
Chrysene	12.66	95
Benzo(b)fluoranthene	6.59	97
Benzo(k)fluoranthene	2.12	89
Benzo(a)pyrene	1.10	94
Indeno(1,2,3-cd)pyrene	4.83	109
Dibenz(a,h)anthracene	0.41	112
Benzo(g,h,i)perylene	5.39	91

the average results for each compound in mass fraction, which correspond to nanograms of PAH found per milligram of SRM 1650b, and the recovery percentage of the 16 target compounds.

The EPA criterion of recovery was selected, which means that recovery must fall between 60% and 120% to be acceptable [33]. In the present work, all the compounds exhibit a recovery within the allowed range, except for anthracene, fluoranthene and benzo(a)anthracene, for which higher recoveries are noticed.

**Fig. 3.** Total PAH in duplicate experiments from pyrolysis operating under different fuel concentrations.

It should be mentioned that the mass fraction sum found of both anthracene and phenanthrene corresponds to the total sum of NIST certified value for these compounds, although individual values for each fraction do not match with those reported by NIST. The most likely reasons are that the mass spectrum of these compounds is very similar with the same base ion and small difference

**Fig. 4.** Individual total PAH in duplicated experiments from pyrolysis operating under different fuel concentrations and reaction temperature of 1223 K.

between their retention times are found. This fact caused a small overlap between their peaks. Similar problems were observed by Ballesteros et al. [9,16] in experiments for determining PAH associated to biofuel soot, since it was not possible to assign accurately the area of the two PAH with the same monitoring ion due to limited chromatographic resolution. Therefore, these values were shown together in all the results.

Regarding to the validation of other compounds, the trials carried out clearly show that the developed method can give reliable quantitative results for most of the EPA-PAH. This was demonstrated by the recoveries higher than 82% most of the cases.

5. Analysis of samples from pyrolytic processes

In this section, the characterization of samples formed from acetylene pyrolysis in a tubular quartz reactor is shown. Experiments using three different inlet acetylene concentrations (10,000 ppmv, 20,000 ppmv and 30,000 ppmv) have been carried out by keeping the pyrolysis temperature constant at 1223 K. Each experiment was repeated twice for checking the repeatability of the method by using real samples.

Fig. 3 shows the total PAH evolution, which refers to the sum of all concentration of PAH found in either the XAD-2 resin (proceeding from the gas phase) and adsorbed on soot. The results present a good repeatability, evidencing that, for a given reaction temperature, the increase in the acetylene concentration favors the total PAH formation.

The individual total PAH concentration, calculated as the individual sum of each PAH concentration found in either the XAD-2 resin and adsorbed on soot, exhibits a good repeatability (Fig. 4). Naphthalene is the compound with higher variability in the 2 repetitions for all conditions, which may be explained due to its high volatility.

Fig. 4 shows that under all conditions, the compounds with higher concentration were naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene, which belong to compounds with two to four aromatic rings or lighter PAH within the EPA-PAH. The only exception was acenaphthene, which was observed in concentrations close to the detection limit, as previously showed by other authors [45], who used similar experimental conditions but different analytical methods.

6. Conclusions

A methodology for quantifying PAH from pyrolytic processes, including both those of the gas phase and adsorbed on soot, has been developed and optimized. The methodology includes classical Soxhlet extraction, concentration under rota-evaporation and subsequent analysis using GC–MS. It has been developed for characterizing and quantifying the PAH listed by the EPA as priority pollutants formed in hydrocarbon pyrolysis experiments.

Results using Printex-U and SRM 1650b show that the developed and optimized method can be successfully applied for PAH analysis, with high precision and reliability for obtaining quantitative data for most of the 16 PAH evaluated. The outcomes of anthracene, fluoranthene and benzo(a)anthracene should be cautiously considered when similar methods are used for EPA-PAH determination.

Analyses of real samples formed under pyrolysis processes of acetylene at different inlet concentration show that it is possible to achieve repeatability in the results, and find reliable amount of target compounds in spite of the complex matrices evaluated (soot).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2013.01.065>.

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