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Determination of PAHs in airborne particles by accelerated solvent extraction and large-volume injection–gas chromatography–mass spectrometry

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Abstract

A sensitive and automated method is presented for the determination of polycyclic aromatic hydrocarbons (PAHs) in airborne particulate matter. The procedure includes extraction of PM10-bound PAHs by accelerated solvent extraction (ASE) followed by gel permeation chromatography (GPC) clean-up, and large-volume programmable temperature vaporizer (PTV–LV) injection coupled to GC–MS. The limit of detection (LOD) of the whole method, based on a signal-to-noise ratio (S/N) of 3:1, ranged from 0.26 pg m^{-3} to 3 pg m^{-3} when air volumes of 760 m^3 are collected.

The hexane–acetone mixture (1:1, v/v) gave the best recoveries when ASE parameters were fixed at 125 °C, 1500 psi, and a total time of 10 min. The recoveries for all PAHs tested ranged from 96% to 103%, rates similar to those obtained by the Soxhlet reference method.

To improve the sensitivity, 70 μL were injected. The PTV–LV injection settings were optimized using a statistical design of experiments, including a screening 2^4 full factorial design and a further central composite design. A sensitivity increase from 10 to 50 times was achieved as compared with the conventional 2 μL splitless injection.

The method was validated with the standard reference material SRM 1649a and applied to real PM10 samples from the monitoring network of the Regional Valencia Government (Spain).

The analytical performance of the method shows that it is appropriate to monitor PAHs levels in ambient air according to European Union Directives. In addition, the method can be used when a high sensitivity is required.

Keywords: PAHs; Ambient air; PM10; Accelerated solvent extraction; Large-volume injection; Design of experiments

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous semivolatile organic pollutants formed by the incomplete combustion of organic matter and are generated whenever fossil fuels or vegetation are burned. Concern with the occurrence of these compounds in the environment is well justified, as they are ubiquitous in ambient air and because some of them are known to be mutagenic or carcinogenic [1,2].

It is a well-known fact that atmospheric PAHs are partitioned between particulate matter and the gas phase [3]. The most volatile compounds are present almost exclusively in the gas phase, while the PAHs with 3 or 4 rings (vapor pressure $\approx 10^{-6}$ Torr to 10^{-8} Torr) can have significant fractions in both the gas and particulate phases. The largest and stronger carcinogenic PAHs (5- and 6-ring) are predominantly associated with particles (vapor pressure $\approx 10^{-11}$ Torr), especially their fine size range with an average diameter lower than 2.5 μm.

The highest concentrations of atmospheric PAHs can be found close to large industrial sites and in urban areas, due to vehicle emissions [4,5]. Traffic-related exposure studies on PAHs showed that the levels of this pollutants in urban areas varied between 0.05 ng m^{-3} and 910 ng m^{-3} [6]. In rural background sites levels of selected PAHs between 0.004 ng m^{-3} and 0.2 ng m^{-3} have been reported [3].

The European Union requires continous air-quality monitoring with long-term assessment of benzo(*a*)pyrene (BaP), used as a marker for carcinogenic risk of PAHs in ambient air, and other

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relevant PAHs that include at least: benzo(*a*)anthracene (BaA), benzo(*b*)fluoranthene (BbFA), benzo(*j*)fluoranthene (BjFA), benzo(*k*)fluoranthene (BkFA), indeno(1,2,3-*cd*)pyrene (IcdP), dibenzo(*a,h*)anthracene (DahA) and fluoranthene (FA) [7]. The Council Directive 2004/107/EC establishes a target value for BaP of 1 ngm^{-3}, and a long-term objective of 0.1 ngm^{-3}, applying to the BaP content in the particulate matter fraction with an aerodynamic diameter lower than 10 μm (PM10).

The PAHs extraction from airborne particulate matter sampled on PM10 filters is usually performed using Soxhlet [8], sonication [9] or shake-flask extraction [10]. These routine methods are time and solvent consuming.

It is widely recognized that accelerated solvent extraction (ASE) gives recoveries comparable to those obtained with Soxhlet and other techniques in use. This technique increases the speed of the extraction process with low solvent consumption [11,12]. Despite this, it has been scarcely used for the extraction of PAHs from PM10 filters [13].

The chromatographic detection of PAHs is usually carried out by liquid chromatography with fluorescence detection (HPLC–FLD) [9] or by gas chromatography with mass spectrometric detection (GC–MS) [14–16]. The former has a high sensitivity but presents an important disavantage: the lack of unambiguous confirmation of the identity of the analytes. GC–MS avoids this disadvantage but provides limits of detection significantly higher than those provided by HPLC–FLD.

Recently, several studies have been reported in which large-volume injection (LVI) methods were used for the GC determination of trace pollutants, such as phenols [17], chloroanilines [18], polychlorinated dibenzo-*p*-dioxins [19] or polybrominated diphenyl ethers [20]. The LVI technique enables significant improvement of overall sensitivity of the analytical method. Instead of the maximum volume of about 2 μl that can be injected when using a conventional technique such as splitless injection, with LVI injection volumes from 30 μl to 100 μl can be used [21]. Typical LVI injectors are programmable temperature vaporisers (PTV) [22].

The PTVs are complex systems that comprises many experimental variables that need to be optimised before its use in an analytical procedure. The optimization of the PTV system can be an intricate process that can be simplified by using experimental design [23]. Two-level factorial designs (FD) and central composite designs (CCD) have been used and preferred to one-factor-at-a-time to optimise analytical methods [24,25]. This approach provides a method for the simultaneous investigation of multiple variables, estimating any interaction among them, and requires few experiments to complete the optimization.

The low concentration of organic pollutants in airborne particulate matter is a great challenge to analytical chemists. Because PAHs are found in low concentrations in PM10, a highly sensitive technique is needed, mainly in studies at rural background sites or in studies where lower air volumes (<30 m^3) are collected, such as indoor studies [26,27] or archived $PM_{2.5}$ filter studies [10].

The aim of the present study was to develop a sensitive procedure for the determination of PAHs in airborne particulate matter at trace level. The procedure includes extraction of PM10-bound PAHs by ASE followed by a clean-up step through gel permeation chromatography (GPC) and the chromatographic detection of PAHs by using PTV–LVI–GC–MS. The method was applied to samples of PM10 filters collected from the monitoring network of the Regional Valencia Government (Spain).

2. Experimental

2.1. Reagents

The analytical standards FA, BaA, BbFA, BjFA, BkFA, BaP, DahA, IcdP and the deuterated chrysene D12 (Chrys D12), pyrene D10 (Pyr D10), benzo(*k*)fluoranthene D12 (BkFA D12) and perylene D12 (Per D12) were supplied by Dr. Ehrenstorfen GmbH (Augsburg, Germany). Standard solutions were prepared by dilution in hexane and stored in capped amber vials at −20 °C. Dichloromethane, acetone, diethyl ether and hexane of analytical grade were purchased from Scharlau (Barcelona, Spain). Hyflo Super Cel®, diatomaceous earth from Aldrich (Steinheim, Germany). Standard Reference Material (SRM) 1649a "Urban Dust" was provided by National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). This is an atmospheric particulate material collected in an urban area and is intended for use in evaluating analytical methods for the determination of selected PAHs and other pollutants in atmospheric particulate material and similar matrices.

The experimental designs were performed and evaluated using the Minitab® Release 14 statistical software from Minitab Inc. (Birmingham, UK), which was also employed for statistical data manipulation.

2.2. Sampling and site characterization

PM10 were collected using a large-volume sampler from Digitel (Madrid, Spain) using quart fiber filters of 150 mm of diameter from Schleicher & Schuell Microscience GmbH (Dassel, Germany). Seven sample sites included in the PM10 monitoring network of the Regional Valencia Government (Generalitat Valenciana), and located in different urban and rural areas of the Comunitat Valenciana (Spain) were selected. Particles were collected during November–December, 2004, using a sampling flow of 30 $m^3\,h^{-1}$, with a total volume of filtered air ranging from 740 m^3 to 760 m^3.

To perform the PM10 determination, a micro balance Mettler-Toledo MX5 from Metller-Toledo Inc. (Bedford, MA, USA) was used. PM10 were obtained by weighting the quart fiber filters using a standard procedure [28].

2.3. Sample extraction

After PM10 determination, the filters were divided into two parts using ceramic scisors. After that, each part was spiked with 125 μl of a surrogate solution containing BkFA D12 and Pyr D10 (1000 ng mL^{-1}) and extracted separately by Soxhlet and ASE.

The Soxhlet extraction of PM10 filters and SRM 1649a samples were carried out by an extraction system B-811from Büchi

(Manchester, UK), and involves an 18-h extraction of the analytes using 200 mL of diethyl ether–hexane (1:9, v/v) as the extraction solvent [29].

The extraction of PAHs from PM10 filters was carried out using an accelerated solvent extraction system (ASE 200, Dionex, Sunnyvale, CA, USA) equipped with 22 mL stainless steel extraction cells. The extraction of samples was performed using the acetone–hexane (1:1, v/v) solvent mixture. Samples were introduced in 22 mL stainless-steel cells containing a cellulose filter in the cell outlet, and the cell refilled with Hyflo Super Cell®. The extraction conditions were as follows: oven temperature, 125 °C; pressure, 1500 psi; 5-min heat-up time; two static cycles; static time, 5 min. The flush volume amounted to 60% of the extraction cell volume. The extracted analytes were purged from the sample cell using pressurized nitrogen (125–150 psi) for 1 min.

Afterwards, the extracts were concentrated under a gentle strem of N_2 at 40 °C and re-dissolved in 700 μL of dichloromethane.

2.4. Gel permeation chromatography clean-up

For both, ASE and Soxhlet extracts, a GPC clean-up was used. The Waters Gel Permeation Chromatography Clean Up System was employed, integrated by a Waters 515 high-pressure liquid chromatography pump, a Waters 717 sample input module, tandem columns Envirogel GPC clean up 19 mm × 150 mm and 19 mm × 300 mm, and a Waters 2487 UV detector (254 nm), together with a Gilson FC 204 Fraction Collector. To concentrate the extracts, a TurboVapII Concentration Workstation from Zymac (Hopkinton, MA, USA) was used.

The experimental conditions were as follows: a mobile phase of methylene chloride, a flow rate of 5 mL min^{-1}, and a volume injection of 700 μL. The collected fractions extended from 14 min to 19 min. Before each multiple-sample procedure, the GPC was calibrated by establishing an elution profile with a calibration solution which consisted of corn oil, *bis*(2-ethylhexyl)phthalate, methoxychlor, perylene [30] The calibration chromatograms were examined to ensure that the relative retention times (RRTs) and peak shapes were as expected.

The collected fractions were evaporated under nitrogen flow at 40 °C, and re-dissolved in 200 μL of a solution containing Chrys D12 and Per D12 (50 ng mL^{-1} in hexane) as internal standards prior to their analysis by GC–MS.

2.5. Chromatographic determination

Chromatographic analyses were performed on a Trace GC-ion trap MS spectrometer from Thermo-Finnigan (San Jose, CA, USA). Separation was carried out on a BPX5 capillary column (SGE Scientific, Ringoes, NJ, USA), 30 m × 0.25 mm i.d., 0.25 μm film thickness, with a fused silica retention gap, 1.5 m × 0.32 mm i.d. (SGE Scientific, Ringoes, NJ, USA). High-purity helium (99.999%) was employed as carrier gas. Programmed temperature vaporization–large-volume injection (PTV–LVI) was carried out using a BEST PTV from ThermoFinnigan and a Combi Pal Autosampler programmable temperature vaporizing injector from CTC Analytics (Zwingen, Switzerland). Data were collected with Xcalibur software data process system.

Large volume introduction into a PTV injector can be done in three different modes [22]: (i) *at-once*, (ii) *speed controlled injection*, and (iii) *multiple injection*. The first two modes are used with the BEST PTV. In the *at-once* mode the sample is introduced at relatively high speed, whereas with the *speed controlled injection* the sample is introduced at a rate that is theoretically equal to the evaporation rate. To simplify the optimization process we used the *at-once* injection at a speed of 100 μL s^{-1}.

The GC temperature program was: initial 70 °C, hold 4 min; rate 15 °C min^{-1} to 100 °C, hold 6 min; rate 6 °C min^{-1} to 280 °C, hold 14 min. PTV injection conditions were as follows: injection volume, 70 μl; injection temperature, 35 °C; vaporisation ramp, 14 °C s^{-1}; vaporisation temperature, 120 °C; transfer and vaporisation ramps, 14 °C s^{-1}; transfer temperature, 280 °C; cleaning temperature, 300 °C; split flow, 25 mL min^{-1}; and vaporizing, transfer and cleaning times of 2.0, 2.0, and 5.00 min, respectively. The mass spectrometer was operated in the electron impact mode (EI) using 70 eV ionization voltage. The ion source temperature was 250 °C and the GC–MS interface was set to 280 °C. The analyses were performed by SIM

Table 1
PAHs compounds analyzed including some important physical and analytical parameters

Compound[a]	Symbol	No. of rings	Boiling point (°C)	Vapor pressure (Pa) at 25 °C[b]	Target SIM ions (*m/z*) (amu)	R.T.[c] (min)
Fluoranthene	FA	4	375	2.00×10^{-3}	200, **202**	30.08
Benzo(*a*)antracene	BaA	4	400	2.80×10^{-5}	**226**, 228	36.59
Benzo(*b*)fluoranthene[d]	BbFA	5	481	6.70×10^{-5}	250, **252**	40.86
Benzo(*j*)fluoranthene	BjFA	5	480	2.00×10^{-6}	250, **252**	40.86
Benzo(*k*)fluoranthene[d]	BkFA	5	480	1.30×10^{-8}	250, **252**	40.98
Benzo(*a*)pyrene	BaP	5	496	7.30×10^{-7}	250, **252**	42.40
Indeno(1,2,3-*c,d*)pyrene[d]	IcdP	6	536	1.30×10^{-8}	274, **276**	49.69
Dibenzo(*a,h*)anthracene[d]	DahA	5	524	1.30×10^{-8}	**274**, 276	50.16

[a] Characteristic ions for surrogate and internal standards: chrysene D12 (i.s.) (236, 240); phenantrene D10 (i.s.) (188, 189); perylene D12 (i.s.) (260, 264, 265); pyrene D10 (208, 212) and benzo(*k*)fluoranthene D12 (260, 264, 265).
[b] As listed by WHO–ICPS [28].
[c] Typical retention time (R.T.) varies according to column condition, age, and exact length.
[d] Vapor pressure at 20 °C.

detection mode using the target ions shown in Table 1. Confirmation criteria for the detection of PAHs should include the following: (a) retention time for two monitored ions for a given analyte should maximize simultaneously ±0.1 s, with signal-to-noise ratio equal to or higher than 3 for each diagnostic ion; (b) the ratio between the two monitored ions should be within 15% of the theoretical value. Quantitation was performed by internal standard calibration using a six-point regression line ranging from 1 ng mL^{-1} to 100 ng mL^{-1}.

3. Results and discussion

3.1. Optimization of the PTV–LV injection

PTV injection can be divided into four phases: injection, vaporization, transfer and cleaning. Each of these phases has different factors that can affect the efficiency of the PTV–LV injector. Taking into account our preliminary studies, four factors were selected as potentially affecting the injection efficiency and as aids in defining the experimental field: injection temperature (T_{inlet}), vaporisation temperature (T_{evap}), vaporisation time ($time_{evap}$) and the flow during the evaporation step (flow). For all the experiments the transfer temperature was fixed at 280 °C in splitless mode for 2 min, and the cleaning temperature was kept at 300 °C for 5 min with the split valve open (300 mL min^{-1}).

3.1.1. Screening design

A full factorial design 2^4 was chosen as a screening method to estimate the relative influence of the four aforementioned factors and their possible interactions on the analytical response, taken as arbitrary units of peak area. The experimental run order was randomized to reduce the effect of extraneous or "nuisance" variables. The values corresponding to the high and low levels taken by each variable are listed in Table 2. An analysis of variance (ANOVA) was performed on the design to assess the significance of the model. The estimated effects of four main factors and six two-way interactions, and their statistical significance at 95% confidence level ($P < 0.05$), are shown in Table 2.

The T_{inlet} has a negative effect because the change of this variable from the low to the high level produces a decrease of the response for the seven PAHs. However, only for the most volatile compounds, FA and BaA, is it statistically significant ($P < 0.05$). This means that a high temperature of injection can produce losses of the aforementioned compounds.

The effect of $time_{evap}$ is always positive (the change from low to high level produces an increase in the response) and is statistically significant for six PAHs. However, FA, the most volatile of PAHs tested, is not affected by this factor.

The T_{evap} and flow were found to be significant for only one (BkFA) and two (BbFA and BaP) compounds, respectively. Moreover, some significant interactions between factors were observed: T_{inlet}–T_{evap}; T_{evap}–flow; T_{evap}–$time_{evap}$. The most relevant of those factors is the latter, as it is statistically significant for all PAHs studied.

It can be concluded that both main variables and second-order interactions affect PTV–LVI performance of PAHs analysed by GC–MS. These results of screening design led the four variables to be considered for further optimization process.

3.1.2. Central composite design (CCD)

The study and optimization of factors having significant effects on the PTV–LV injection are appropiately performed through a central composite design. This type of experimental design permits the response surface for each compound to be

Table 2
Estimated effects and *P*-values ($\alpha = 0.05$) of the four main factors and the six two-way interactions of the full factorial design used in the optimization of the PTV injector (coded units)

Factor	Level	
	Low	High
T_{inlet} (°C)	35	80
T_{evap} (°C)	50	105
$Time_{evap}$ (min)	0.2	2
Flow (mL min^{-1})	50	200

Factor	Effect (*P*-value)						
	FA	BaA	BbFA[a]	BkFA	BaP	IcdP	DahA
T_{inlet}	−18908 (0.005)	−17556 (0.046)	−7102 (0.459)	−7553 (0.153)	−574 (0.819)	−1415 (0.296)	−2279 (0.349)
T_{vap}	−3219 (0.443)	−6669 (0.361)	−8998 (0.356)	−12536 (0.038)	−5402 (0.072)	−1136 (0.931)	−2820 (0.57)
$Time_{evap}$	7429 (0.113)	26003 (0.011)	39649 (0.007)	18875 (0.008)	12168 (0.004)	5302 (0.007)	10038 (0.006)
Flow	2633 (0.526)	12619 (0.116)	23351 (0.046)	7693 (0.147)	6937 (0.033)	2418 (0.102)	4808 (0.081)
T_{inlet}–T_{vap}	22507 (0.002)	22774 (0.019)	13891 (0.177)	5383 (0.284)	3035 (0.257)	1199 (0.368)	649 (0.781)
T_{inlet}–$time_{evap}$	2884 (0.489)	8909 (0.237)	8789 (0.366)	9994 (0.077)	4906 (0.094)	1661 (0.229)	1939 (0.420)
T_{inlet}–flow	3560 (0.399)	13114 (0.105)	6920 (0.470)	10173 (0.073)	2164 (0.404)	114 (0.929)	261 (0.910)
T_{vap}–$time_{vap}$	−10000 (0.049)	−27489 (0.009)	−26192 (0.032)	−24257 (0.003)	−10595 (0.007)	−3911 (0.023)	−8198 (0.014)
T_{vap}–flow	−7675 (0.104)	−16906 (0.051)	−15810 (0.134)	−17948 (0.010)	−7503 (0.025)	−3045 (0.054)	−4522 (0.096)
$Time_{evap}$–flow	−5982 (0.182)	−10661 (0.169)	−10734 (0.279)	−5128 (0.305)	−3307 (0.222)	−1363 (0.311)	−2614 (0.289)

Fixed parameters of the PTV–LVI: transfer temperature, 280 °C; splitless time, 2 min; cleaning temperature, 300 °C; cleaning flow, 300 mL min^{-1} for 5 min.
[a] BbFA + BjFA.

Table 3
Experimental conditions and response (peak area) of the central composite design used for optimization of PTV–LV injection in GC–MS analysis of PAHs

Run	T_{inlet} (°C)	T_{evap} (°C)	$Time_{evap}$ (min)	Flow (mL min^{-1})	FA	BaA	BbFA	BkFA	BaP	IcdP	DahA
1	50	80	1.1	125	406257	299156	279649	186711	84533	38859	41740
2	50	80	1.1	125	421870	302034	277948	212916	95132	40680	49186
3	80	80	1.1	125	426184	319770	319343	231348	106777	46869	50301
4	65	100	0.65	75	442481	293444	269821	127870	74772	21266	21805
5	65	100	1.55	75	440410	313028	276809	171216	83663	26827	27477
6	35	100	0.65	175	358007	250835	178485	183122	66465	24191	23320
7	50	80	2	125	464675	370551	373214	253699	119049	43106	47353
8	50	80	1.1	125	451123	325384	310737	216264	93386	41255	41312
9	65	60	1.55	75	68334	208551	290117	227371	93033	31946	35747
10	65	60	1.55	175	44377	160806	287874	199943	88387	33239	32738
11	65	60	0.65	175	46769	137484	229995	182357	76075	32376	32607
12	35	60	1.55	75	510333	391550	374697	240114	109500	38852	40002
13	35	100	0.65	75	697293	429717	329897	252496	105895	33686	35304
14	35	60	1.55	175	483062	390552	371059	274168	126088	48056	46952
15	65	100	0.65	175	59776	196552	286730	191045	82242	29639	32063
16	65	60	0.65	75	65232	177402	247188	170520	71180	27069	28088
17	50	120	1.1	125	456378	328675	281516	202194	87012	31413	33872
18	50	80	0.2	125	417724	247010	189218	142205	55868	21193	22976
19	50	80	1.1	125	423057	317219	288165	208758	94122	35116	36801
20	50	80	1.1	125	423645	346517	331821	232811	116975	46072	54281
21	65	100	1.55	175	421646	323549	306050	222973	103040	39828	42781
22	35	100	1.55	75	638384	515543	555048	449994	203952	67736	76383
23	50	80	1.1	125	427225	313611	303659	202715	93953	36763	41847
24	50	40	1.1	125	159472	323462	430741	270720	149071	66007	71788
25	50	80	1.1	25	255816	115925	57953	54138	19832	7011	5964
26	35	100	1.55	175	396586	294925	256823	176330	76757	26482	24199
27	35	60	0.65	175	495303	386209	381758	239536	126019	55986	59610
28	50	80	1.1	225	450474	321690	326857	206127	99736	38607	37280
29	20	80	1.1	125	428997	311082	288752	199894	91650	35120	37825
30	35	60	0.65	75	493434	385254	475167	274103	162308	56799	69608
31	50	80	1.1	125	425530	317320	298663	210029	96350	39791	44195

built, and the factor settings or operating conditions that maximize the analyte response exposed on arbitrary units of peak area to be found. The CCD model selected was composed of a full factorial 2^4 design that includes 16 factorial points to which are added 8 axial points and 7 central points, involving a total of 31 randomized chromatographic runs. The values corresponding to every factor in each experiment and the responses for each PAHs compound are shown in Table 3.

The responses were fitted by a multiple regression equation, including second-order (curvature) and interaction terms. Three-dimensional response surface shows the effect of two independent variables on a given response, at a constant value of the other two independent variables. Fig. 1 shows, as an example, some response surfaces obtained by using the model aforementioned for FA, BaP, and DahA.

The following step was to select the factors settings that maximize the PAHs response. This could be done using the "response optimiser" from response surface design in the MINITAB program.

As we have multiple responses (one for each PAHs), and as the response surfaces are different for each compound (see Fig. 1), it is necessary to find a factor setting that simultaneously maximizes the desirability for each response. It must be noticed that the desirability is 0.0 for the lowest values obtained in the CCD; increases as response values increase; and is 1.0 for the highest response obtained in the experiments. For this reason, we maximize a composite desirability, that combines the individual desirability of all the response variables into a single measure, taking into account that all the response variables have the same importance. The optimised factors settings (see Table 4) provide a composite desirability of 0.93.

Table 4
Optimised factor settings and the individual and composite desirability for PAHs determination by PTV–LV–GC–MS

Factor	Optimum
T_{inlet} (°C)	35
T_{evap} (°C)	120
$Time_{evap}$ (min)	2
Flow	25
Compound	**Desirability**
FA	0.73
BaA	0.95
BbFA	1.0
BkFA	1.0
BaP	1.0
IcdP	0.97
DahA	0.87
Composite	0.93

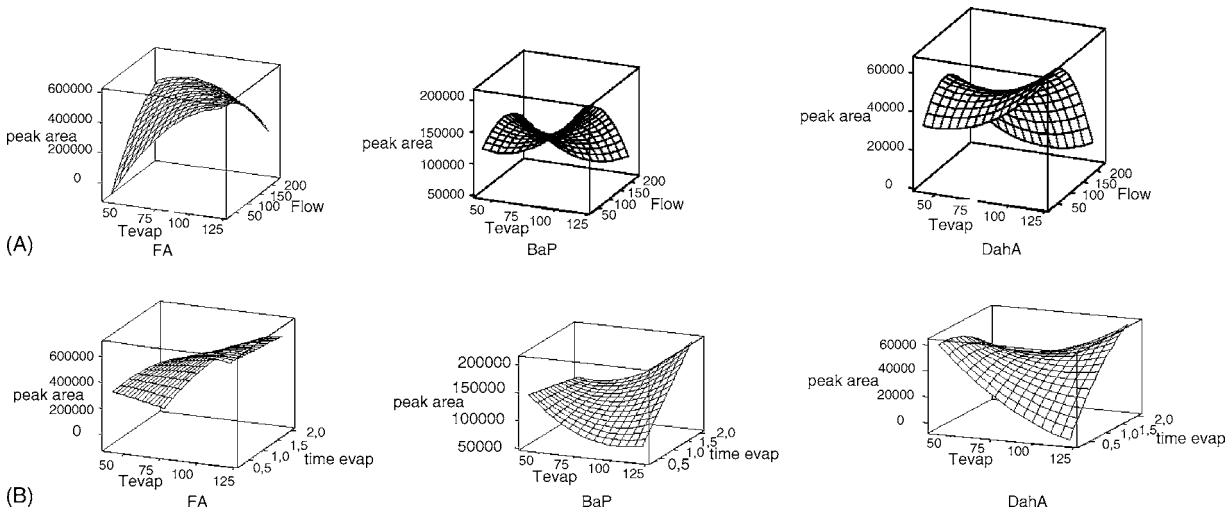

Fig. 1. Response surfaces for FA, BaP, and DahA. Fixed conditions (A) $time_{evap}$: 2 min; T_{inlet}: 35 °C; (B) T_{inlet}: 35 °C, flow: 25 mL min^{-1}.

In short, in the injection step the split valve was open and 70 μL of the sample was introduced into the liner at a temperature of 35 °C (30 °C below the boiling point of hexane). During the evaporation step, the PTV was raised to 120 °C, at 14 °C s^{-1}, for 120 s, to eliminate the solvent, and the solvent was vented through the split valve at a flow of 25 mLmin^{-1}. In the transfer phase, the split valve was closed and the temperature quickly raised (14 °C s^{-1}) to 280 °C in splitless mode for 2 min. Finally, the liner was keep at 300 °C, 5 min, with a flow of 300 mL min^{-1} for cleaning.

We studied the repeatability and linearity of the PTV–LV injector by injecting five series of 6-standars in the range from 5 ng mL^{-1} to 200 ng mL^{-1}. The results are shown in Table 5.

Also, the instrumental limit of detection (i-LOD), defined as the lowest concentration of each PAHs that provides a signal-to-noise value equal or higher than 3 for every target ion (*m/z*), was compared with that obtained injecting 3 μL in the splitless mode. As can be seen in Table 5, the sensitivity achieved using the PTV–LIV was improved from 10 to 50 times as compared with the conventional injection system with similar low relative standard deviation (R.S.D.).

3.2. Extraction of SRM 1649a with ASE and Soxhlet: effect of extraction solvent

The polarity of the extraction solvent should closely match that of the target compounds.

However, in some cases, solvent mixtures of polar and non-polar solvents give higher recoveries than pure ones. Four solvent mixtures, including dichloromethane–acetone (1:1, v/v), hexane–acetone (1:1, v/v), hexane–acetone (4:1, v/v), and diethyl ether–hexane (1:9, v/v) were tested as extraction solvents under the standard operating conditions described in Section 2.3. We selected these ASE operating conditions taking into account our previous experience in the analysis of PAHs by ASE from other environmental matrices [31]. The solvent mixtures were chosen from those used in conventional Soxhlet and ASE methods for the extraction of PAHs [11]. In order to validate the selected extraction settings the extraction experiments were carried out on the SRM 1649a, and the extraction with Soxhlet was used as reference method.

Table 6 illustrates the effect of the solvent on the recovery of PAHs from the SRM 1649a, and shows as

Table 5
Analytical features of the PTV–LV injector and a common split/splitless injector

Compound	PTV							Splitless	
	Regression line[a]					R.S.D.[b] (%)	i-LOD (ng mL^{-1})	R.S.D.[b] (%)	i-LOD (ng mL^{-1})
	a	s_a	*b*	s_b	R^2				
FA	−0.019	0.067	0.0223	0.0004	0.991	2.6	0.1	2.5	5
BaA	−0.3674	0.104	0.0482	0.00110	0.990	2.9	0.1	2.6	1
BbFA + BjFA	−0.7912	0.186	0.0915	0.00197	0.991	2.0	0.1	2.1	25
BkFA	−0.368	0.1306	0.0616	0.00139	0.990	3.9	0.1	3.5	25
BaP	−0.4687	0.089	0.0502	0.0009	0.993	1.6	0.1	2.0	25
IcdP	−0.2078	0.068	0.0387	0.0007	0.993	2.2	1	2.3	25
DahA	−0.3351	0.076	0.0373	0.0008	0.991	2.5	1	2.3	25

a: Intercept of the regression line; *b*: slope of the regression line; s_a: standard deviation of the intercept; s_b: standard deviation of the slope; R^2: coefficient of determination; i-LOD: instrumental limit of detection. R.S.D.: relative standard deviation.

[a] From five series of 6-standars in the range 5–200 ng mL^{-1}.

[b] From five injections of a 20 ng mL^{-1} standard.

Table 6
Effect of different solvent mixtures on the extraction of PAHs by MAE from a SRM 1649a material

Compound	Certified concentration[a]	Recovery (%) ± S.D.				
		ASE[b]				Diethyl ether–hexane (1:9)
		Hexane–dichloromethane (1:1)	Hexane–acetone (4:1)	Hexane–acetone (1:1)	Diethyl ether–hexane (1:9)	Soxhlet
FA	6.45 ± 0.18	81 ± 9	86 ± 9	103 ± 1	94 ± 2	80 ± 10
BaA	2.208 ± 0.073	87 ± 7	103 ± 7	103 ± 3	102 ± 6	98 ± 5
BbFA + BjFA	6.45 ± 0.64	86 ± 3	83 ± 3	102 ± 4	88 ± 2	90 ± 6
BkFA	1.913 ± 0.031	91 ± 7	99 ± 9	101 ± 6	100 ± 9	93 ± 5
BaP	2.509 ± 0.087	95 ± 6	80 ± 6	97 ± 4	81 ± 7	95 ± 7
IcdP	3.18 ± 0.72	85 ± 4	87 ± 4	100 ± 2	86 ± 5	80 ± 6
DahA	0.288 ± 0.023	87 ± 9	92 ± 9	96 ± 6	82 ± 2	80 ± 10

$n = 3$. S.D.: standard deviation.
[a] The dispersion is expressed as expanded uncertainty at 95% level of confidence.
[b] ASE operating conditions: temperature, 125 °C; pressure, 1500 psi; heat-up time, 5 min; static time, 5 min; cycles, 1.

well the recoveries obtained by the Soxhlet methodology.

Statistical treatment of the data was given on the eight PAHs investigated. As the Soxhlet has been reported as a reference method for the extraction of PAHs from soils and other environmental matrices, the recoveries of the ASE methods with the four solvent mixtures were compared with those of the Soxhlet method, using a two-sample *t*-test approach, at 95% confidence level [32]. The PAHs recoveries were not statistically different to the Soxhlet ($P > 0.05$) for all the solvent mixtures employed in ASE, except for IcdP extracted by hexane–acetone (1:1, v/v), which gave recoveries in ASE higher than those obtained by Soxhlet. Consequently, the mixture hexane–acetone (1:1, v/v) was chosen as extractant solvent.

For all PAHs tested, the recovery of the ASE method calculated from repeated analyses of the SRM 1649a ranged from 96% to 103%, thus evidencing the applicability of the developed method.

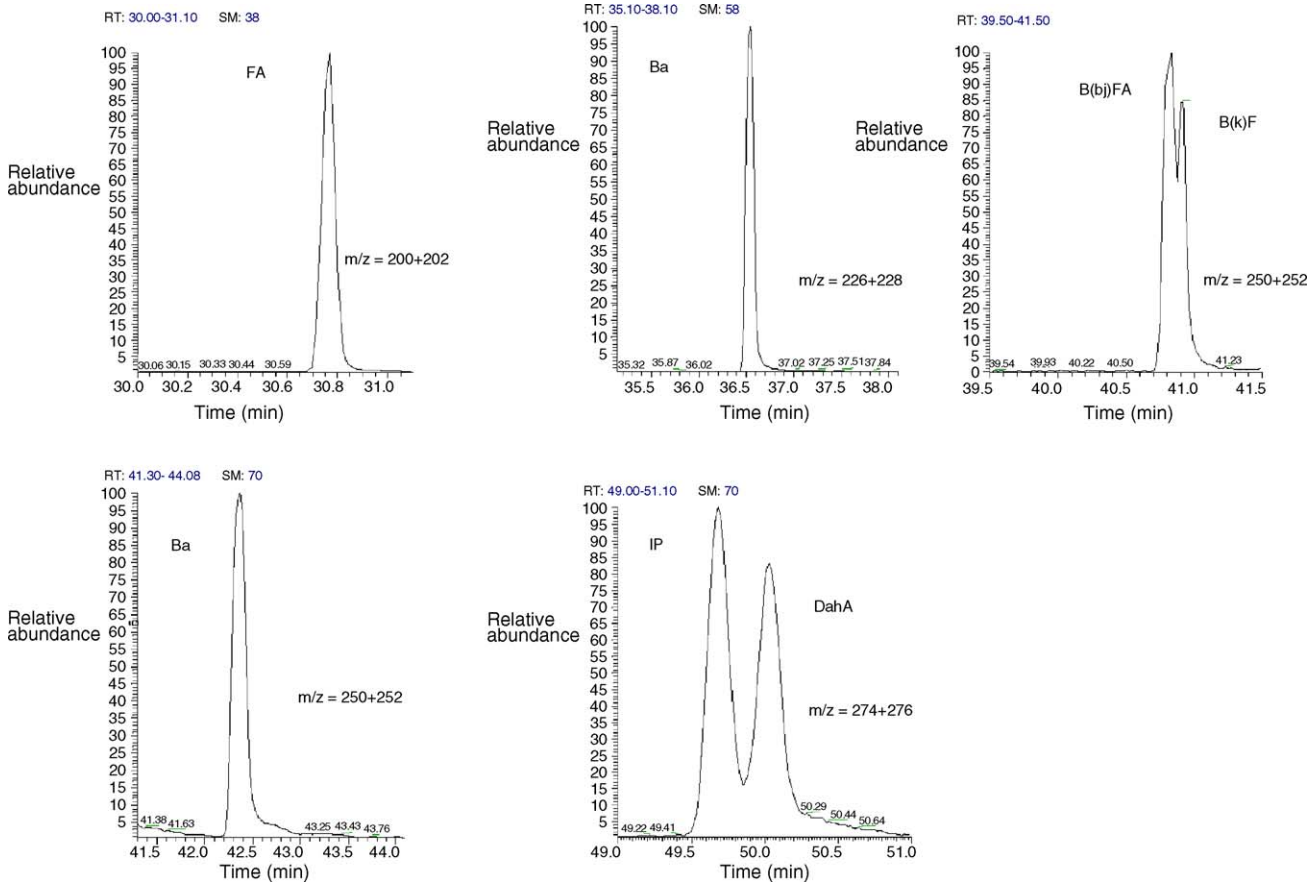

Fig. 2. SIM ion chromatogram of the PAHs obtained for a field PM10 sample extracted by ASE as purified by GPC.

Table 7
Determination of PAHs (ng m^{-3}) in PM10 samples by PTV–LV–MS after ASE and Soxhlet extraction

	Sample number							Regression line				
	1	2	3	4	5	6	7	R^2	Intercept		Slope	
	43[a]	37[a]	19[a]	26[a]	44[a]	47[a]	19[a]		lcl	ucl	lcl	ucl
FA	0.308 (0.25)	0.072 (0.072)	0.51 (0.441)	0.226 (0.265)	0.202 (0.181)	0.198 (0.225)	0.168 (0.179)	0.94	−0.252	0.106	0.545	1.030
BaA	0.383 (0.442)	0.064 (0.047)	1.025 (0.740)	0.373 (0.284)	0.195 (0.158)	0.393 (0.378)	0.160 (0.123)	0.93	−0.06	0.151	0.490	0.951
BbjFA[b]	0.968 (0.860)	0.073 (0.069)	0.945 (1.205)	0.520 (0.495)	0.335 (0.310)	0.356 (0.325)	1.348 (1.250)	0.93	−0.245	0.240	0.682	1.312
BkF	0.893 (1.230)	0.071 (0.06)	0.405 (0.290)	0.409 (0.512)	0.165 (0.210)	0.191 (0.170)	1.244 (1.320)	0.94	−0.226	0.176	0.851	1.496
BaP	0.480 (0.560)	0.076 (0.100)	1.082 (0.900)	0.613 (0.560)	0.271 (0.239)	0.417 (0.348)	0.812 (0.552)	0.91	−0.099	0.233	0.475	1.012
IP	0.05 (0.069)	0.015 (0.006)	0.205 (0.158)	0.095 (0.054)	0.051 (0.020)	0.053 (0.036)	0.158 (0.126)	0.91	−0.033	0.058	0.229	1.079
DahA	0.053 (0.04)	0.147 (0.125)	1.521 (1.061)	0.745 (0.551)	0.406 (0.386)	0.492 (0.515)	2.106 (2.111)	0.95	−0.287	0.229	0.666	1.158

Concentrations within parenthesis correspond to Soxhlet extraction; lcl: lower confidence level 95%; ucl: upper confidence level 95%.
[a] PM10 concentration (μg m^{-3}).
[b] BbjFA = BbFA + BjFA.

The limit of detection (LOD) of the whole method, based on a signal-to-noise ratio (S/N) of 3:1, ranged from 0.26 pg m^{-3} to 3 pg m^{-3} when air volumes of 760 m^3 are collected.

This LOD is lower than those provided by others GC–MS methods [10,33] and HPLC-fluorescence methods [34]. The method is sufficiently sensitive to montoring these PAHs in samples of background rural sites were levels of 0.004 ng m^{-3} have been reported [3].

3.3. Determination of PAHs in PM10 field samples

We tested the performance of the ASE method with real samples from seven sites included in the PM10 monitoring network of the Regional Valencia Government.

Table 7 shows the results found using the ASE and the Soxhlet procedures. To compare the two methods we used a regression line [32]. As can be seen in Table 7, for all PAHs tested the coefficient of determination $R^2 > 0.90$, and for six out seven PAHs the intercept and the slope do not differ significantly from zero and 1, respectively. Only for BaA the upper confidence limit was slightly lower than 1. This means that there are no systematic differences when both methods are compared, and consequently, both methods give similar results in real sample analysis.

The accuracy of the whole procedure for the routine analysis of PM10 samples is guaranteed by the use of surrogates (Pyr D10 and B*k*F D12) added before the extraction and clean-up of the filters, permitting a continuous quality control of the results.

Fig. 2 illustrates a chromatogram of a real PM10 sample obtained by the developed procedure. Concerning the concentration of BaP in Valencia dust samples, it can be concluded that six out of seven samples analysed had lower concentration than the target level (1 ng m^{-3}) established by the Council Directive 2004/107/CE.

4. Conclusions

An ASE procedure followed by LVI and GC–MS has been developed for analysis of PAHs in airborne matter. The analytical performance of the method shows that it is suitable to monitoring the PAHs concentrations in air ambient as established by the European Union. In addition, our method can be used when a high sensitivity is required, as occur in studies where lower air volumes (<30 m^{-3}) are collected, such as indoor studies or archived $PM_{2.5}$ filter studies.

For an individual sample, the extraction by ASE is faster than the conventional Soxhlet extraction and reduces the solvent consumption.

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