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Simultaneous Sampling of Vapor and Particle-Phase Carcinogenic Polycyclic Aromatic Hydrocarbons on Functionalized Glass Fiber Filters

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ABSTRACT

The sampling of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere is often performed on filters, which retain only aerosol particles, disregarding the vapor fraction; after the filter, an adsorbent (e.g., polyurethane foam, PUF, or styrene/divinylbenzene, XAD) is sometimes used for sampling vapors not retained from the filter. However, the use of an adsorbent may lead to many disadvantages: contaminations, analysis time and costs, and size problems when developing automated or personal samplers. In this work, a functionalized glass fiber filter for the simultaneous sampling of aerosol particles and vapor fraction is presented for the sampling of PAHs in air. A low sampling efficiency was observed for 3 ring PAHs, but all carcinogenic PAHs (according to IARC) were totally retained on functionalized filters. On the other hand, a comparison with normal filter sampling was performed, and results obtained confirm that >10% of benzo(a)pyrene can be lost from normal filters. Together with size reduction, another advantage of the functionalized filter is an enhancement in the extraction and purification recovery.

Keywords: Polycyclic aromatic compounds; PM₁₀; Ambient samplers; SVOC; Aerosol sampling and transport.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of air pollutants of great interest because of their toxicity and widespread sources (Kim *et al.*, 2013). As well as many other organic pollutants (e.g., polychlorinated biphenyls, dioxins, brominated flame retardants, phthalates, pesticides, perfluorinated substances etc.) PAHs belong to the group of semivolatile organic compounds (SVOCs), according to the WHO definition (WHO, 1989). In the atmosphere, SVOCs are widely known to be partitioned between aerosol particles and a vapor phase, on the basis of their vapor pressure (Pankow, 1994; Tzapakis and Stephanou, 2005).

Even though the gas/particle partitioning is well known, PAHs sampling is often performed only on filters (usually quartz fiber filters, glass fiber filters or teflon filters) (Mastral *et al.*, 2003; Li *et al.*, 2009; Shi *et al.*, 2010; Herlekar *et al.*, 2012; Da Limu *et al.*, 2013), disregarding the vapor fraction, which is not retained on the filter itself (Pandey *et al.*, 2011). Even legislations follow this approach: EU Directive

2004/107/EC defines the concentration of benzo(a)pyrene as the target value for all PAHs, and requires its sampling on a simple filter media according to EN 12341 method. This approach is justified by the widespread belief that the vapor fraction of the most harmful PAHs with 5–6 aromatic rings is negligible (Liu *et al.*, 2001a; Lu and Chen, 2008; Pandey *et al.*, 2011; Slezakova *et al.*, 2011; Szulejko *et al.*, 2014). However, it has been observed that, even for benzo(a)pyrene, the vapor fraction can sometimes constitute a significant amount of the total concentration (Possanzini *et al.*, 2004; Temime-Roussel *et al.*, 2004; Masih *et al.*, 2012; Delgado-Saborit *et al.*, 2014). Additionally, a significant amount of pollutants could be desorbed from the aerosol particles collected on the filter during the sampling, (Zhang and McMurry 1991, Delgado-Saborit *et al.*, 2014).

In order to collect vapors not retained by the filter, a solid sorbent can be used downstream the filter itself. The most commonly used adsorbents are polyurethane foam cartridges (PUF) and poly(styrene-divinylbenzene) porous particles (commercially known as XAD-2™). PUF is an efficient sorbent even for the most volatile PAHs: thanks to its relatively high capacity, low cost and small impedance, it is widely used in air sampling (Park *et al.*, 2002; Bi *et al.*, 2003; Du Four *et al.*, 2005; Miller *et al.*, 2010; Anastasopoulos *et al.*, 2012; Kavouras *et al.*, 2015; EPA method TO-13A). XAD is a valid alternative to PUF, due to its high adsorption

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capacity for aromatic compounds (Bartkow *et al.*, 2004a, b; Ré-Poppi and Santiago-Silva 2005; Masih *et al.*, 2012; Liu *et al.*, 2014). The filter-XAD configuration has also been investigated for personal samplers (Preuss *et al.*, 2006) and for indoor air sampling (Chuang *et al.*, 1991). Combinations of PUF and XAD downstream the filter are also used (Iavicoli *et al.*, 2007; Liu *et al.*, 2010; Xie *et al.*, 2014).

In summary, the combined filter-adsorbent cartridge sampler allows to collect the total amount of PAHs in the air, but these adsorbent materials have some limitations that should not be neglected: the clean-up and the extraction of both PUF and XAD require a large consumption of time and solvents (in order to overcome this problem, solvent bubbling has been proposed; Portet-Koltalo *et al.*, 2011); if adsorbents are reused, there are serious risks of contamination (thermally regenerable adsorbents, such as polydimethylsiloxane and Tenax™ might be a possible solution to this problem, as highlighted by Liu *et al.* (2001b), Wauters *et al.* (2008) and Lazarov *et al.* (2013). Moreover, adsorbent cartridges are bulky compared to filters, and difficult to be used in personal and automated samplers. A disposable device able to simultaneously act both as a filter and as an adsorbent would prevent all the mentioned disadvantages, allowing a simultaneous sampling of both vapor- and particle-phase PAHs, leading to faster and cheaper analyses, lower contamination risks, and making personal and automated samplers easier to be developed.

Several commercially available disposable devices are known for liquid matrices, comprising ENVI-Disk™ (Sigma Aldrich™, Saint Louis, MO, USA), Empore™ disks (3M™, Saint Paul, MN, USA) and Atlantic SPE disks™ (Horizon Technology™, Salem, NH, USA).

ENVI-Disk™ is a filter with adsorbent microparticles dispersed on it. The filter is made of glass fibers, and the adsorbent microparticles are silica microspheres grafted with octadecyl and octyl functional groups, for ENVI-18 DSK disks and ENVI-8 DSK, respectively. ENVI-Disk™ are commonly used for solid phase extraction (SPE) of organic compounds from liquid samples, and PAHs can be extracted from water using these devices (Urbe and Ruana, 1997). However, to this day, there are no studies in which ENVI-Disks™ are used for the sampling of SVOCs in air.

Empore™ are constituted by adsorbent particles incorporated in a teflon network. Empore™ disks are commonly used for SPE of organic compounds from liquid matrices (Van Loon *et al.*, 1996), and have been used as a low volume active air sampler of organic micropollutants (Sanchez *et al.*, 2003; Tollbäck *et al.*, 2006) including PAHs (Tollbäck *et al.*, 2008). However, as well as for ENVI-Disk™, no studies are available for the use of Empore™ in commercial PM sampler.

The adsorbent material in Atlantic™ SPE disks is not incorporated in a teflon network but is located between two layers of glass fiber. These devices are used for SPE of organic compounds from liquid matrices (Leandro *et al.*, 2006), but have never been used for the sampling in air of SVOCs.

Aim of this work is to investigate a new sampling method for PAHs, based on an innovative filtering and

adsorbing device: a functionalized glass fiber filter. In the proposed method, commercial glass fiber filters are functionalized with phenyl moieties and used for the atmospheric sampling of PAHs.

METHODS

Functionalization and Characterization of Filters

Glass microfiber filters GF/D™ (47 mm diameter, Sigma Aldrich™) were heated at 400°C for 24 h and then soaked in a NaOH (analytical grade, Sigma Aldrich™) 2M aqueous solution, at 25°C for 24 h; the filters were then rinsed with water, acetone and toluene (Super Purity Solvent, Romil™, Cambridge, UK), and functionalized with a solution of phenyltriethoxysilane (PTES, Sigma Aldrich™) 5% in toluene at 80°C for 24h. Finally, filters were rinsed with toluene and acetone. Both functionalized and standard GF/D filters were analyzed by thermogravimetric and differential thermal analysis, using a calorimeter/thermobalance SDT Q600™ (TA Instruments™, New Castle, DE, USA). Analyses were performed with a heating rate of 5 °C min⁻¹ in air (SIAD™, purity 99.9995%).

Air Sampling

Ten parallel experimental air samplings (sampling time: 24 h) were performed in a sub-urban location (Monterotondo, 00015, Rome, Italy) both in summer (June 2014, minimum temperature +14°C, maximum temperature +35°C) and in winter (January 2015, minimum temperature -2°C, maximum temperature +17°C). Two Skypost PM™ HV samplers (Tecora™, Fontenay sous Bois Cedex, France), equipped with a PM₁₀ inlet were used with a flow rate of 38.33 L min⁻¹. In particular, one air sampler was used with functionalized filters, the other with normal GF/D™ filters. Downstream the filters, a cylindrical polyurethane foam cartridge (density 0,022 g cm⁻¹, 1 cm diameter per 5 cm length; Tisch Environmental™, Cleves, OH, USA) was used to collect vapors not retained from filters (Park *et al.*, 2002; Bi *et al.*, 2003; Du Four *et al.*, 2005; Miller *et al.*, 2010; Pandley *et al.*, 2011, Anastasopoulos *et al.*, 2012). The sampling geometry is described by Fig. 1.

The same parallel sampling experiments were performed using ENVI-Disk™ (Sigma Aldrich™, Saint Louis, MO, USA), Empore™ disks (3M™, Saint Paul, MN, USA) and Atlantic SPE disks™ (Horizon Technology™, Salem, NH, USA).

Sample Analysis

The following PAHs were considered: acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3,c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene. Higher molecular weight PAHs (e.g., dibenzopyrenes and coronene) were not included because they were expected to be totally collected on normal filters (Park *et al.*, 2002; Ohura *et al.*, 2004; Tsapakis and Stephanou, 2005, Ravindra *et al.*, 2006, Ras *et al.*, 2009).

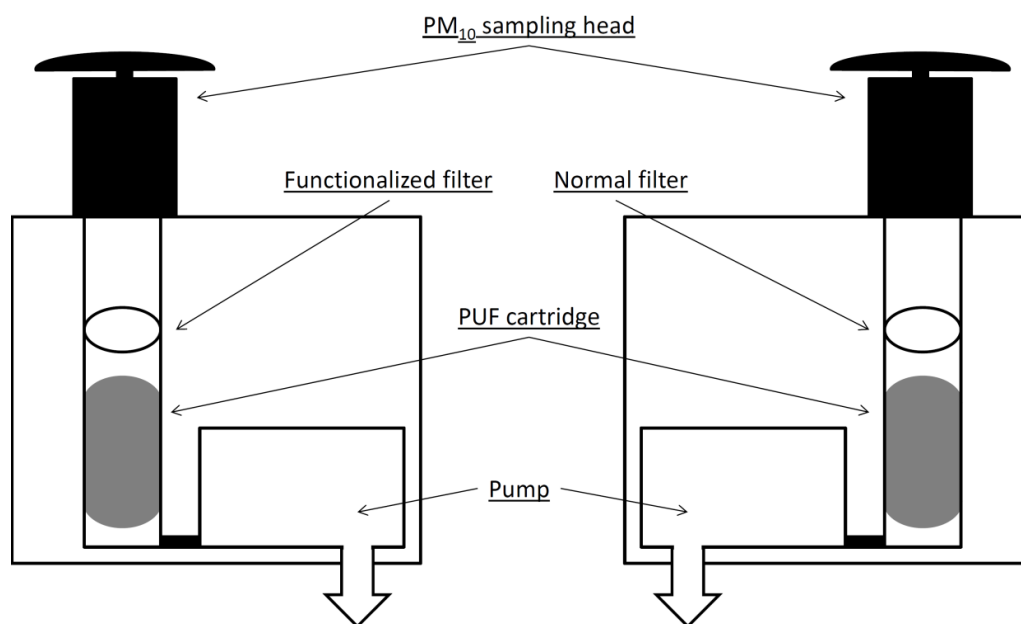


Fig. 1. Sampling geometry for normal and functionalized fiber filters.

PAHs were quantified by GC/MS with isotopic dilution method: after the sampling and before the extraction, filters and PUF were spiked with 5 ng of perdeuterated PAHs (L429-IS Internal Standard D-IPA Stock Solution, Wellington Laboratories™, Guelph, Canada) as an internal standard. In order to evaluate the sampling efficiency, filters and PUF were separately analyzed. PAHs were Soxhlet-extracted in hexane for 24 h. Extracted samples were concentrated by rotary evaporator (40°C, $3.00 \cdot 10^{-4}$ Pa) to 3–5 mL, and then automatically purified by gel permeation chromatography and concentrated, using an AccuPrep MPST™ & AccuVap Inline™ (J2 Scientific™, Columbia, MO, USA) (Guerriero *et al.*, 2009).

GC/MS analysis was performed on an Ultra Trace™ gas chromatograph coupled to a TSQ™ mass spectrometer (Thermo Fischer Scientific™, St Peters, MO, USA) used in single ion monitoring (SIM) mode. The column Meta-XLB™ (60 m length, 0.25 mm internal diameter, 0.25 μ m film thickness; Teknokroma™, Barcelona, Spain) was used for the separation, and He (99.9995% purity) was used as carrier gas. The temperatures for the injector, transfer line and ion source were 260°C, 280°C and 250°C, respectively. The oven temperature program was the following: isothermal at 60°C for 1 min; gradient at 20 °C min⁻¹ up to 250°C; isothermal at 250°C for 10 min; gradient at 15 °C min⁻¹ up to 300°C; isothermal at 300°C for 15 min; gradient at 5 °C min⁻¹ up to 325°C; isothermal at 325°C for 10 min.

Each native PAH was quantified using its perdeuterated isotologues as internal standard, except for acenaphthene (quantified using perdeuterated acenaphthylene), fluoranthene, anthracene (quantified using perdeuterated phenanthrene), pyrene (quantified using perdeuterated fluoranthene) and benzo(e)pyrene (quantified using perdeuterated benzo(a)pyrene).

Extraction and Purification Recovery

In order to calculate the extraction and purification recovery, 5 ng of recovery standard (L429-RS Recovery Standard D-IPA Stock Solution, Wellington Laboratories™) were added before injection in GC/MS. Recovery was calculated as the percentage ratio between the internal standard (added before the extraction) and the recovery standard (added before the injection in GC/MS). Perdeuterated acenaphthene was used for calculating the recovery of acenaphthylene and phenanthrene; perdeuterated pyrene was used for calculating the recovery of fluoranthene, benzo(a)anthracene and chrysene; perdeuterated benzo(e)pyrene was used for calculating the recovery of benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, perylene, indeno(1,2,3,c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene.

RESULTS AND DISCUSSION

Characterization of Filters

Fig. 2 shows the simultaneous differential thermal and thermogravimetric analysis of both a functionalized filter (Fig. 2(a)) and a blank What™ an GF/D glass fiber filter (Fig. 2(b)). A rapid weight loss associated with a calorimetric peak can be observed at 225°C, in the thermal analysis of the functionalized filter, while this signal is absent in the blank filter analysis. Such a weight loss associated to a calorimetric peak in the range 150–300°C can be associated to the functionalization of the silica surface (Bugrayev *et al.*, 2008; Cataldo *et al.*, 2008). An organic carbon content of 6% can be estimated using the thermogravimetric analysis (Dufaud *et al.* 2003; Cousiniè *et al.*, 2007). It can be also observed that the signal associated to desorption of water (below 100°C) is lower for the functionalized filter: this phenomenon can also be attributed to the functionalization, which lead to a less hygroscopic surface.

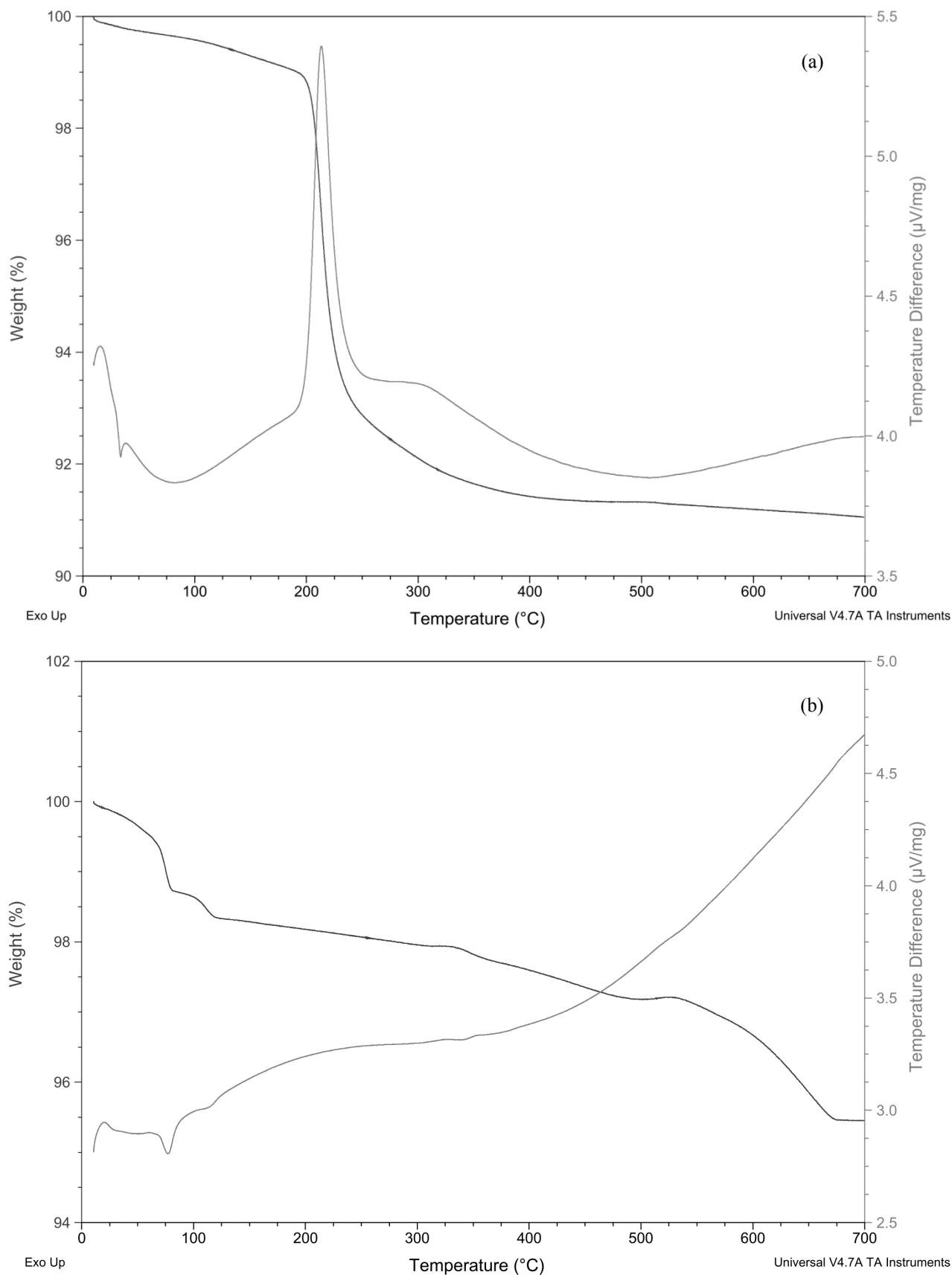


Fig. 2. Thermogravimetric and differential thermal analysis of (a) a functionalized glass fiber filter and (b) blank glass fiber filter ($5\text{ }^{\circ}\text{C min}^{-1}$ in air). The black line represents weight variations as a function of temperature (thermogravimetric analysis), while the grey line identifies the temperature difference measured (differential thermal analysis).

Sampling efficiency

The sampling efficiency (E%) was calculated by the following equation (1), where Q_f and Q_a are the amount of PAHs collected on the filter and on the adsorbent (i.e., PUF), respectively:

$$E\% = \frac{100Q_f}{Q_f + Q_a} \quad (1)$$

Table 1 shows a comparison of the sampling efficiencies of standard and functionalized filters. During the summer, as expected, the sampling efficiency is reduced, due to the higher atmospheric temperature. Even if a total sampling of 3-ring PAHs cannot be performed on the proposed device, PAHs from benzo(a)anthracene to benzo(g,h,i)perylene are almost totally retained on functionalized filters: this result is very interesting since all carcinogenic PAHs (according to IARC reports, 1987; 2010; 2012) can be sampled without using an adsorbent cartridge (e.g., PUF or XAD), leading to a more compact sampling line and easier extraction procedures.

Compared to method involving Empore disk™ proposed by Tollbäck *et al.* (2008), a very higher flow rate can be used (38.33 L min⁻¹ instead of 1.2 L min⁻¹). The same applies to PAH sampling methods based on Tenax adsorbents proposed by Wauters *et al.* (2008) and Lazarov *et al.* (2013), in which the flow rate was 0.1 L min⁻¹ and 0.098–0.254 L min⁻¹, respectively.

Comparison with Glass Fiber Filters

As for standard glass fiber filters, data on sampling efficiency are in good agreement with literature (Park, 2002; Tsapakis and Stephanou, 2005; Ravindra *et al.*, 2006; Ras *et al.*, 2009; Xie *et al.*, 2014), and confirm that a significant

amount of PAHs is not retained on normal filters. It is very important to remark that, in the summer period, significant losses from the filter are observed even for the heaviest PAHs, including also the most toxic benzo(a)pyrene (more than 10% collected on the PUF downstream the filter). Similar results were obtained by Ravindra *et al.* (2006) and by Tsapakis and Stephanou (2005), who found 7% and more than 8% of benzo(a)pyrene downstream the filter, respectively.

These losses are the effect of two different phenomena: gas/particle partitioning and desorption artifacts. Denuder sampling experiments (Possanzini *et al.*, 2004; Temime-Russel *et al.* 2004; Masih 2012; Delgado-Saborit, 2014) have shown that the vapor fraction of 4- and 5-rings PAHs cannot always be neglected: since vapors are not retained on the filter, they are collected on the PUF cartridge. Furthermore, particulate PAHs can be partially desorbed from aerosol particles during the sampling (Zhang and McMurphy, 1991; Delgado-Saborit *et al.*, 2014) and collected on the PUF cartridge. As expected, both the phenomena are enhanced during the summer (Ravindra *et al.*, 2006; Tsapakis and Stephanou, 2005), leading to a lower efficiency of normal glass fiber filter.

In summary, it was confirmed that significant amounts of carcinogenic PAHs are lost from normal filters, while the proposed functionalized fiber filters allow to minimize these losses without using a PUF of a XAD cartridge. This allows to reduce time and costs of analyses, and to reduce the size of the sampling line.

As a further consideration, an apparent disadvantage of the functionalized fiber filters is the lack of information on the gas/particle partitioning. Actually, it is important to remark that vapor/particle partitioning cannot be simply calculated by sampling on a normal filter followed by an adsorbent: indeed, compounds originally sorbed on aerosol

Table 1. Sampling efficiency of functionalized and normal glass fiber filters. IARC classification stands for “carcinogenic to humans” (1), “probably carcinogenic to humans” (2A), “possibly carcinogenic to humans” (2B) and “not classifiable as to its carcinogenicity to humans” (3).

Compound	Rings	IARC Classification	Summer sampling		Winter sampling	
			Normal filter	Functionalized filter	Normal filter	Functionalized filter
Acenaphthylene	3	(not classified)	(5 ± 6)%	(26 ± 7)%	(7 ± 5)%	(31 ± 4)%
Acenaphthene	3	3	(5 ± 8)%	(24 ± 4)%	(9 ± 6)%	(34 ± 7)%
Fluorene	3	3	(8 ± 6)%	(35 ± 8)%	(12 ± 7)%	(41 ± 5)%
Phenanthrene	3	3	(12 ± 4)%	(41 ± 6)%	(18 ± 4)%	(48 ± 5)%
Anthracene	3	3	(15 ± 6)%	(42 ± 5)%	(21 ± 5)%	(52 ± 4)%
Fluoranthene	4	3	(19 ± 11)%	(52 ± 7)%	(29 ± 6)%	(56 ± 7)%
Pyrene	4	3	(35 ± 6)%	(62 ± 7)%	(40 ± 5)%	(72 ± 6)%
Benzo(a)anthracene	4	2B	(71 ± 7)%	(76 ± 5)%	(83 ± 7)%	> 99%
Chrysene	4	2B	(81 ± 5)%	(85 ± 6)%	(87 ± 6)%	> 99%
Benzo(b+j)fluoranthene	5	2B	(88 ± 9)%	(95 ± 4)%	> 99%	> 99%
Benzo(k)fluoranthene	5	2B	(88 ± 6)%	> 99%	> 99%	> 99%
Benzo(e)pyrene	5	3	(85 ± 3)%	> 99%	> 99%	> 99%
Benzo(a)pyrene	5	1	(87 ± 6)%	> 99%	> 99%	> 99%
Perylene	5	3	(92 ± 7)%	> 99%	> 99%	> 99%
Indeno(1,2,3,c,d)pyrene	5	2B	(93 ± 3)%	> 99%	> 99%	> 99%
Dibenzo(a,h)anthracene	5	2A	(96 ± 7)%	> 99%	> 99%	> 99%
Benzo(g,h,i)perylene	6	3	(98 ± 4)%	> 99%	> 99%	> 99%

particles are partially desorbed from the filter and then retained on the adsorbent, leading to an overestimation of the vapor fraction (Zhang and McMurry, 1991; Goriaux et al., 2006; Delgado-Saborit et al., 2014); moreover, vapor phase compounds can be adsorbed on the filter, leading to an underestimation of the vapor fraction (Hart and Pankow, 1994; Xie et al. 2014).

Therefore, sampling vapors and particles on a single device would not lead to a loss of information on the atmospheric vapor/particle partitioning, since this information is anyway not available with a conventional filter/adsorbent sampling: an accurate vapor/particle partitioning measurement can only be performed with a denuder (Possanzini et al., 2004; Temime-Russel et al., 2004; Masih et al., 2012; Delgado-Saborit et al., 2014).

Extraction and Purification Recovery

In order to compare the analytical performances of these new functionalized fiber filters with classical sampling devices (standard filters and PUF cartridges), extraction and purification recovery was evaluated. Results are shown in Table 2. The extraction of PAHs from PUF was confirmed to be less efficient than the extraction from glass fiber filters. This is due to the strong interactions between PAHs and polyurethane. Conversely, higher recoveries were observed from functionalized fiber filters, without significant differences with standard glass fiber filters. Thus, functionalized fiber filters can be handled in laboratory as the normal fiber filters. This may be probably due to a weaker interaction between PAHs and functionalized fiber filters. Functionalized fiber filters give higher recoveries when compared to ENVI™ (78–93%, Urbe and Ruana, 1997) and Empore™ disks (80–130%, Tollbäck et al., 2008).

Comparison with ENVI™, Empore™ and Atlantic™ Filters

SPE devices described in the Introduction paragraph, including ENVI™, Empore™ and Atlantic™ filters could be used for a simultaneous sampling of vapor and particle phase PAHs. Unfortunately, the high impedance of these devices led to a shutdown of the air sampler pump, when used at the flow rate of 38.33 L min⁻¹. Of course, it is possible to perform an air sampling with a lower flow rate

with these filters, but in these conditions the sampling of PM₁₀ and PM_{2.5} cannot be performed on the considered commercial air samplers. Nevertheless, lower flow rates lead to higher sampling time to reach detection limits. In a previous work by Sanchez et al. (2003), Empore™ disks have been successfully used for the sampling of nitroaromatic compounds, with a relatively high flow rate: the flow rate was set to 20 L min⁻¹, yielding a sampling capacity of 15 L min⁻¹, as a result of the backpressure of the Empore™ disk. Such a pressure drop would not be acceptable for the sampling of PAH, because it is demonstrated that pressure drop is the main cause of volatilization artifacts (Goriaux et al., 2006; NIOSH, 2014).

A more specific issue occurred for ENVI™ disks: microparticles on which analytes are adsorbed can be lost during the time elapsing between sampling and analysis, since microparticles are not bonded to the filter. This is not a problem in SPE from water media, for which this device is designed, but it is a serious problem when it is used in air sampling. Finally, the thickness of Empore™ and Atlantic™ disks is higher than 2 millimeters, so that they can hardly be inserted in commercial air sampling instruments.

All the mentioned difficulties are confirmed in the previous work of Tollbäck et al. (2008), in which Empore™ disks have been used for the sampling of PAHs: it was necessary to design a dedicated sampling line, with a specific pump (VDE 0530 KNF, Neuberger, Freiburg, Germany), and the sampling flow rate was only 1.2 L min⁻¹.

In light of what we have shown up to this point, it was not possible to perform a direct comparison between ENVIDisks™, Empore™, and Atlantic SPE disks™, because all of these devices cannot be used with a flow rate of 38.33 L min⁻¹, which is commonly used for PAHs sampling. Sampling at a lower flow rate would make lose the aerodynamic selection of aerosols and would provide not comparable results in terms of sampling efficiency (which is a function of the face velocity, according to McDow and Huntzicker, 1990). Hence, a direct comparison between functionalized fiber filters and commercial SPE filters cannot be shown. However, it is possible to state that none of those systems (ENVIDisk™, Empore™ disks, Atlantic SPE disk™) allows to perform a PM sampling on common air samplers.

Table 2. Average recoveries of PAHs from the sampling devices used.

Compound	PUF cartridges	Functionalized filters	Normal filters
Acenaphthylene-D ₈	(41 ± 9)%	(34 ± 15)%	(36 ± 12)%
Phenanthrene- D ₁₀	(61 ± 7)%	(52 ± 12)%	(57 ± 9)%
Fluoranthene-D ₁₀	(58 ± 7)%	(72 ± 9)%	(76 ± 5)%
Benzo(a)anthracene-D ₁₀	(69 ± 9)%	(85 ± 3)%	(94 ± 5)%
Chrysene-D ₁₂	(60 ± 6)%	(75 ± 3)%	(80 ± 7)%
Benzo(b)fluoranthene- D ₁₂	(68 ± 5)%	(81 ± 5)%	(83 ± 4)%
Benzo(k)fluoranthene-D ₁₂	(75 ± 6)%	(85 ± 7)%	(80 ± 3)%
Benzo(a)pyrene-D ₁₂	(71 ± 3)%	(83 ± 3)%	(89 ± 8)%
Indeno(1,2,3,c,d)pyrene-D ₁₂	(96 ± 9)%	(98 ± 11)%	(95 ± 9)%
Dibenzo(a,h)anthracene-D ₁₄	(67 ± 4)%	(65 ± 6)%	(50 ± 3)%
Benzo(g,h,i)perylene-D ₁₂	(78 ± 7)%	(93 ± 7)%	(91 ± 11)%
Average PAHs	(68 ± 11)%	(75 ± 11)%	(76 ± 14)%

CONCLUSIONS

A functionalized fiber filter was developed and tested for the simultaneous sampling of vapor-phase and particle-phase carcinogenic PAHs in the atmosphere. Unlike other commercial SPE disks, the proposed devices are compatible with the high sampling flow rates of PM samplers. All carcinogenic PAHs were efficiently collected on functionalized filters, while normal filters showed significant losses.

Sampling PAHs on functionalized fiber filters allows to avoid the use of PUF, XAD and other adsorbents, leading to a more compact and cost-saving sampling method. Therefore, personal and automated samplers might be developed without the encumbrance of the adsorbent cartridge. Moreover, since functionalized fiber filters are disposable, blank artifacts are lower and smaller limits of detection and quantification can be reached. Compared to PUF cartridges, the extraction of analytes from these devices leads to higher recoveries and lower solvent consumption, because they are smaller and the adsorptive interaction is weaker.

Finally, functionalized fiber filters are likely to be suitable for the sampling of other SVOCs, maintaining all the mentioned advantages. In conclusion, the functionalized fiber filters described are a novel, promising device for the sampling of SVOCs, and interesting applications on automated samplers and personal samplers are expected.

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DISCLAIMER

The authors declare that there is no conflict of interest.

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