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Determination of particulate polycyclic aromatic hydrocarbons in ambient air by gas chromatography-mass spectrometry after molecularly imprinted polymer extraction

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ABSTRACT

A solid phase extraction procedure (SPE) is described for the quantitative analysis of polycyclic aromatic hydrocarbons (PAHs) in atmospheric particulate matter (PM), as ubiquitous environmental pollutants routinely measured in air quality monitoring. A SPE cartridge was used based on a molecular imprinted polymer (MIP-SPE) properly tailored for selective retention of PAHs with 4 and more benzene fused rings. The performance of the clean-up procedure was evaluated with the specific concern of selective purification towards saturated hydrocarbons, which are the PM components mostly interfering GC analysis of target PAHs. Under optimized operative conditions, the MIP-SPE provided analyte recovery close to 95% for heavier PAHs, from benzo(α)pyrene to benzo(ghi)perylene, and close to 90% for four benzene rings PAHs, with good reproducibility (RSDs: 2.5%–5.9%). Otherwise, C₁₇–C₃₂ n-alkanes were nearly completely removed. The proposed method was critically compared with Solid Phase Micro Extraction (SPME) using a polyacrylate fiber. Both methods were successfully applied to the analysis of ambient PM_{2.5} samples collected at an urban polluted site. Between the two procedures, the MIP-SPE provided the highest recovery (R% \geq 93%) for PAHs with 5 and more benzene rings, but lower for lighter PAHs. In contrast, SPME showed a mean acceptable R% value (\sim 80%) for all the investigated PAHs, except for the heaviest PAHs in the most polluted samples (R%: 110%–138%), suggesting an incomplete purification from the interfering n-hydrocarbons.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants, mainly generated during incomplete combustion of organic materials, which are considered po-

tential contributors to adverse health effects, including mutagenicity, genotoxicity and carcinogenicity (Du et al., 2018; Niu et al., 2017; Shen et al., 2018; Sun et al., 2018; Abdel-Shafy and Mansour, 2016; Zhang et al., 2020, 2021). Special attention must be paid to sixteen PAHs designated as priority pollutants from the US Environmental Protection Agency (US EPA) (Keith et al., 2015). Thus, they are routinely monitored in ambient particulate matter (PM), as an essential step for better understanding their fate and exposure to humans

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(Nozière et al., 2015; Masala et al., 2016; Nalin et al., 2018; Wilson et al., 2018). Despite years of effort and the use of the most sophisticated chromatographic available techniques, the accurate determination of PAHs in PM samples is still a challenging task, because PM is a very complex mixture of inorganic and organic components, widely varying in molecular weight, functional groups and polarity, and also because PAHs are commonly present at trace level in the ambient air (mostly 0.1–2 ng/m³) (Ding et al., 2011; Masala et al., 2016; Nyiri et al., 2016). Therefore, the conventional approach for PAH analysis in PM must include processes for pre-separation and pre-concentration of the target compounds from multi-component mixtures (Ramírez et al., 2010; Cochran et al., 2012; Santos et al., 2016; Wilson et al., 2018; Kim et al., 2019).

The widely employed solid phase extraction (SPE) has been found useful for PAHs analysis as a preliminary clean-up step before chromatographic and spectroscopic techniques, in order to separate the whole PAH fraction or discrete fractions based on the number of aromatic rings (Nozière et al., 2015; Kim et al., 2019). SPE cartridge based on molecularly imprinted polymers (MIPs) as sorbent has been found to largely magnify the SPE advantages in terms of extraction efficiency and selectivity (Beltran et al., 2010; Krupadam et al., 2010; Ho et al., 2011; Martín-Esteban et al., 2016). MIPs are highly cross-linked polymers containing molecular recognition elements based on tailored binding sites for a chosen template molecule. A MIP-SPE cartridge has been specifically developed and commercially available for distinctive recognition of PAHs containing 4 and more benzene rings, including highly carcinogenic dibenzo pyrene isomers (Krupadam et al., 2010; Ho et al., 2011; Sun et al., 2017). It has been found that it provides high selectivity, combined with high capacity and excellent mechanical and thermal stability (Beltran et al., 2010; Martín-Esteban et al., 2016). Special attention must be paid in selecting the clean-up protocol, as specific operative conditions are required to achieve the strongest selective interactions with the MIP sorbent, otherwise, the imprinting is pointless.

Solid phase micro extraction (SPME) has been also widely used for PAHs clean-up, as a well-established green technique, since it is a solvent-free alternative for extraction and pre-concentration of the compounds from a variety of matrices (Pawliszyn, 2000; Ballesteros et al., 2009; Menezes and Cardeal, 2011; Basaglia and Pietrogrande, 2012; Li et al., 2015; Naccarato and Tagarelli, 2019). Compared with the laborious SPE procedure, it reduces the number of steps, by combining sampling and pre-concentration in one step, as it permits desorption directly into the injector of the chromatographic system (Pawliszyn, 2000). SPME has been successfully used for quantification of PAHs in different environmental matrices (Basaglia and Pietrogrande, 2012; Al-Alam et al., 2017; Naccarato and Tagarelli, 2019; Resende dos Santos et al., 2019; Naing et al., 2020), including atmospheric PM (Li et al., 2015; Ballesteros et al., 2009; Menezes and Cardeal, 2011).

In this work, a clean-up procedure based on MIP-SPE is described for the analysis of 16 priority pollutant PAHs in atmospheric aerosol, as an original application to this environmental matrix. This study was specifically focused on the selective PAH purification towards saturated hydrocarbons – normal and branched alkanes – which are the PM components mostly interfering GC analysis. The reasons are that they show

very similar retention properties as target PAHs in the most common GC columns and that they are commonly present in urban PM at high concentration levels, as emitted from vehicular traffic and vegetative detritus (C₂₉–C₃₁ odd alkanes) (Ramírez et al., 2010; Chan et al., 2013; Pietrogrande et al., 2014; Lyu et al., 2019; Wang et al., 2019). The MIP-SPE method was compared with the SPME procedure, by highlighting advantages and disadvantages in terms of analyte recovery and selectivity towards interferences. To highlight the relevance of the clean-up procedure in air quality monitoring, the comparative study was carried out on ambient PM_{2.5} samples collected in an urban polluted site, in addition to standard mixtures of target PAHs.

1. Material and methods

1.1. Chemicals and reagents

Methanol (HPLC grades), cyclohexane (HPLC grades), *n*-hexane (HPLC grades) and dichloromethane ≥ 99.99% were purchased from E. Merck (USA) and used as received. Individual standards of each PAH were purchased from Supelco (Bellefonte, PA, USA). The 16 US EPA priority PAHs were investigated: naphthalene (NaP), acenaphthene (AcP), acenaphthylene (AcPy), fluorene (Flu), phenanthrene (PhA), anthracene (AnT), fluoranthene (FluA), pyrene (Pyr), benzo(α)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(α)pyrene (BaP), indeno(1,2,3-cd)pyrene (InP), dibenz(a,h)anthracene (DbA), and benzo(ghi)perylene (BghiP). Individual standards of 15 *n*-alkanes (from C₁₇ to C₃₂) were purchased from Acros Organics (New Jersey, USA).

Stock solutions containing 200 µg/mL of each analyte were prepared by dissolving each PAH in dichloromethane and each *n*-alkane in cyclohexane. Working solutions of PAHs and *n*-alkanes (at 500 ng/mL each) were prepared by dilution with cyclohexane. All solutions were stored at –6°C.

The internal standard solution (EPA 8270 Semivolatile Internal Standard Mix) was supplied by Supelco (Bellefonte, PA, USA). It contains 6 deuterated PAHs at the concentration of 200 µg/mL in dichloromethane, i.e., naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, perylene-d₁₂, 1,4-dichlorobenzene-d₄. A diluted solution at 100 ng/mL was added to the sample to compute the calibration curves and investigate the analytical performance of the method.

1.2. Solid-phase extraction procedure

Commercial SPE cartridges SupelMIP™ SPE-PAHs were supplied by Supelco (Bellefonte, PA, USA). They contained 50 mg of PAH-selective MIP sorbent in a 3 mL volume tube. The optimized cleaning protocol consisted of preconditioning the MIP-SPE cartridge with 2 mL of cyclohexane. Then, sample loading was performed under vacuum at a flow rate of 3 mL/min. The sorbent was washed with 2 mL of cyclohexane and the retained PAHs were eluted with 2 mL of dichloromethane. Eluate was dried under gentle nitrogen flow and reconstituted with 100 µL of cyclohexane. Then, 2 µL of the extract were automatically injected into the GC/MS instrument (Focus GC/PolarisQ

Ion Trap Mass Spectrometer, Thermo-Fisher Scientific, Bellefonte, PA, USA) for analysis.

The procedure was applied to 500 μL of standard mixture of PAHs and *n*-alkanes (100 ng/mL for each compound) prepared in cyclohexane. The method linearity and sensitivity were investigated by computing the calibration curves using a standard mixture of PAHs (six concentration points ranging from 1 to 300 ng/mL). After validation, the extraction procedure was conducted on 500 μL of the cyclohexane extract from $\text{PM}_{2.5}$ real filters.

1.3. Solid phase micro extraction procedure

Two commercial SPME fibers coated with different materials were used in this work: one was coated with polydimethylsiloxane/divinylbenzene (PDMS/DVB, 85 μm), whereas the other was coated with polyacrylate (PA, 65 μm fibers). Both were supplied by Supelco (Bellefonte, USA) and housed in a manual holder.

Following the conditioning guidelines, prior to use, the fibers were conditioned for 30 min in the hot injection port of the gas chromatograph, at 270°C for the PDMS/DVB fiber and at 280°C for the PA fiber. Helium flowrate was nearly 1.0 m/min and the split valve was open, to reduce the amount of impurities entering the column. The fiber blank was tested by thermal desorption (5 min in the injection port) followed by GC analysis to confirm that all compounds were desorbed and prevent the fiber memory effect.

Both SPME fibers were directly immersed in a 20 mL flask containing 2 mL of methanol solution under agitation for 1 hr at room temperature. Then, each fiber was transferred into the GC injection port, where desorption of the analyte occurred for 5 min at 270°C and at 280°C for the PDMS/DVB and PA fibers, respectively. The procedure was investigated on standard mixture of PAHs and *n*-alkanes (at 25 ng/mL each) in methanol. Additionally, 2 mL the methanol extract from $\text{PM}_{2.5}$ real filters were analyzed.

1.4. Real $\text{PM}_{2.5}$ sample collection and preparation

Ambient particulate matter ($\text{PM}_{2.5}$) samples were collected at an urban site in Bologna (Northern Italy) during January to February 2017. Particles were collected on prewashed and prebaked quartz fiber filter (Pall; 9-cm diameter) by a high-volume air sampler operating at a constant nominal flow rate of 500 L/min for 24 hr, to collect an air volume of 720 m^3 . The $\text{PM}_{2.5}$ filters were stored in a freezer (-20°C) in the dark prior to use.

A quarter of the filter was extracted for 30 min in an ultrasonic bath with 15 mL of *n*-hexane:dichloromethane, 30:70 (V/V), solvent mixture. Then, the extracts were filtered using a syringe filter (PTFE 25 mm, 0.22 μm , Kinesis) to remove insoluble particles. The filtrates were evaporated to dryness in a centrifugal vacuum concentrator (miVac Duo Concentrator, Genevac Ltd, Ipswich, UK).

The samples were reconstituted with 500 μL of the extraction solvent, transferred in 2 mL glass vials and dried under gently nitrogen flow. Then, samples were recovered with 100 μL of cyclohexane for direct injection into GC/MS system, or submitted to SPE or SPME clean-up.

Method blank was measured by submitting reagents and blank PM filters to the whole SPE or SPME procedures.

1.5. GC/MS analysis

Chromatographic analyses were performed on a Gas Chromatograph Focus GC (Thermo-Fisher Scientific, Bellefonte, PA, USA) coupled with a mass spectrometry detector PolarisQ Ion Trap Mass Spectrometer (Thermo Fisher Scientific, Bellefonte, PA, USA). The target analytes were separated by a Rxi@-5Sil MS capillary column (5% diphenyl/95% dimethylsiloxane, 30 m length \times 0.25 mm diameter \times 0.25 mm film thickness, Restek, USA). High purity helium (99.999%) was used as the carrier gas at constant flow rate of 1.4 mL/min. For direct injection, 2 μL of sample was injected in the split/splitless injector maintained at 280°C (splitless for 5 min). Oven temperatures for GC were programmed as follows: held at initial temperature of 40°C for 2 min, ramped to 275°C at a rate of 15°C/min, then ramped to 320°C at a rate of 10°C/min and finally held for 10 min.

The GC/MS interface was kept at 280°C. Analysis of target compounds were conducted using electron-impact ionization at 70 eV voltage and source temperature at 250°C. Signal was acquired operating in full-scan mode (40-650 m/z range) and selected ion monitoring (SIM) mode by selecting specific fragments of each target PAH and *n*-alkane (m/z values of the most abundant characteristic ion). The tandem MS was operated in single reaction monitoring (SRM) mode, by using transition parameters (precursor ion, product ion and collision energy) reported in literature. Data acquisition was performed using Thermo Scientific 1.4 X-Calibur program (WestPalm Beach, USA).

2. Results and discussion

2.1. Optimization of the MIP-SPE clean-up procedure

The operative conditions of the MIP-SPE clean-up were optimized, starting from the extraction protocol recommended by the MIP producer: namely, conditioning with 1 mL of cyclohexane, washing interferences with 1 mL of cyclohexane, eluting PAHs with 3 mL of dichloromethane. This study was conducted on laboratory solutions containing 16 PAHs (from NaP to BghiP) and 16 *n*-alkanes (C_{17} to C_{32}) at concentrations of 100 ng/mL of each compound in cyclohexane. Such a concentration has been selected to properly represent the PAH level which may be found in urban air, since it corresponds to concentration of 0.83 ng/ m^3 in the sampled air (under the used operative protocol reported in Section 1.4). Each experiment was repeated in triplicate. For each SPE operative condition, the percentage of recovery (R%) of each target analyte was computed by comparing PAH concentration in solutions after and before the SPE clean-up (based on peaks area of the chromatographic signal).

First, the effect of the solvent volume used for cartridge conditioning was investigated by increasing the cyclohexane volume from 1 to 4 mL, using the recommended solvent volumes for other steps (mean and standard deviation values reported in Fig. 1a, left side). The obtained results clearly show

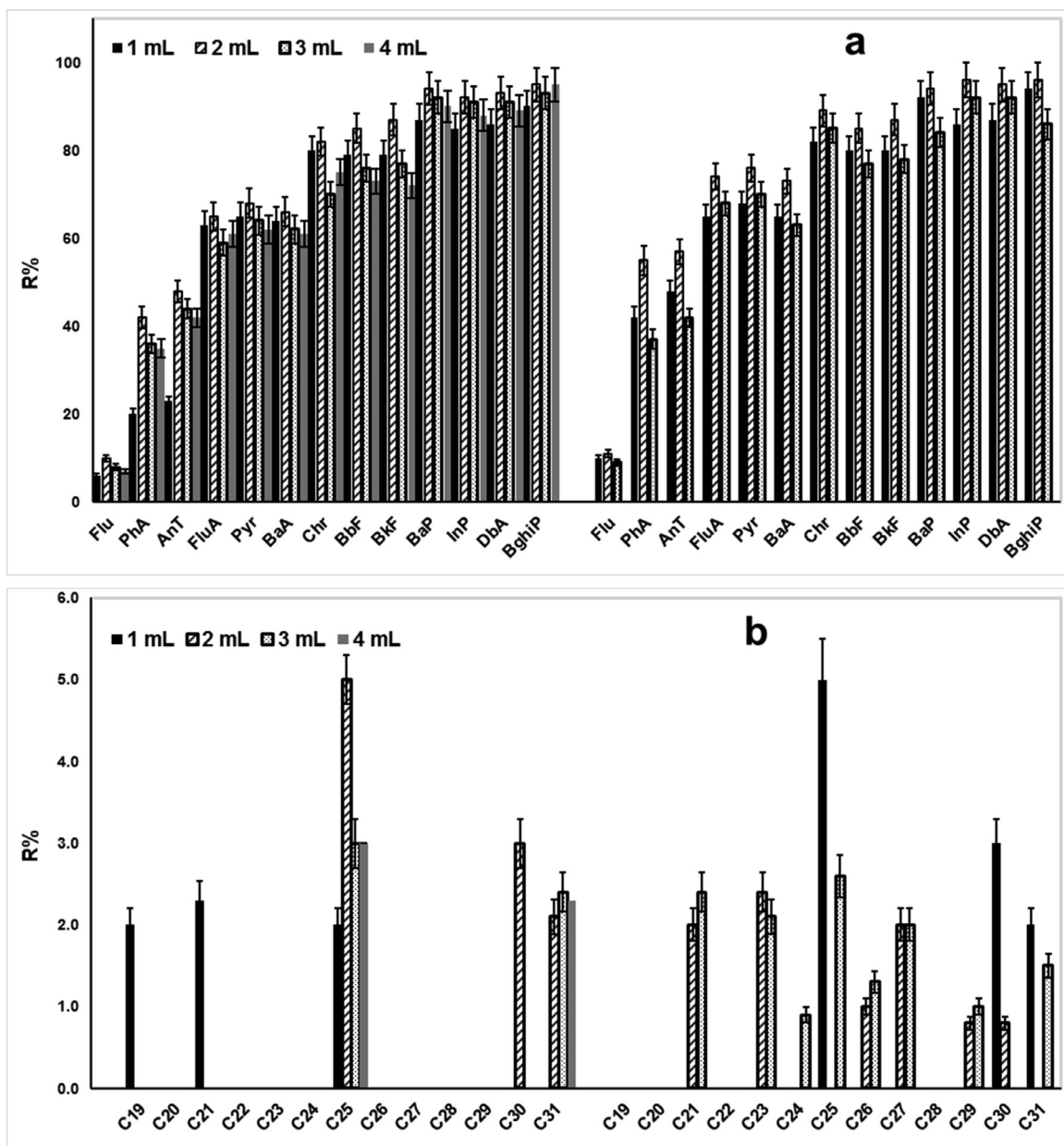


Fig. 1 – Effect of the MIP-SPE operative conditions on the clean-up recovery of the investigated PAHs and *n*-alkanes (100 ng/mL). Bars report mean and standard deviation values ($n = 3$). Left side: effect of varying cyclohexane volume in cartridge conditioning: 1, 2, 3 and 4 mL (washing: 2 mL of cyclohexane; elution: 3 mL of dichloromethane); right side: effect of varying cyclohexane volume for cartridge washing: 1, 2 and 3 mL (conditioning: 2 mL of cyclohexane; elution: 3 mL of dichloromethane). (a) % recovery of PAHs; (b) % recovery of C₁₉-C₃₁ *n*-alkanes.

that the analyte recovery strongly depends on the PAH molecular structure, with values increasing with the number of fused rings in the molecule. In fact, no recovery (NaP, AcPy, AcP) or low values were measured for the lighter PAHs, with unacceptable recovery ($R\% \leq 65\%$) for PAHs with 3 or less benzene fused rings. The clean-up yield increased to achieve the best values higher than 92% for 5 and 6 rings PAHs, i.e., from BaP to BghiP. Overall, the PAHs recovery varied only slightly with the conditioning volume, with mean values for Flu to BghiP terms of 64 ± 29 , 71 ± 25 , 66 ± 25 and 65 ± 25 , when conditioning with 1, 2, 3 and 4 mL, respectively. Thus, the volume of

2 mL yielding the highest recovery (striped bars in Fig. 1a) was used in the following experiments.

Then, the cyclohexane volume for the cartridge washing was optimized by increasing the volume from 1 to 3 mL. Comparing the extraction recoveries obtained (mean and standard deviation values reported in Fig. 1a, right side), we can conclude that 2 mL is the best washing volume to obtain a recovery close to 95% for the heavier PAHs, from BaP to BghiP (striped bars in Fig. 1a).

Finally, the elution step was investigated by measuring the PAHs recovery after elution with increasing dichloromethane

Table 1 – Clean-up recovery (R%) of each target PAH varying dichloromethane volume in cartridge elution: 2, 3 and 4 mL (conditioning: 2 mL of cyclohexane; washing: 2 mL of cyclohexane).

PAHs	2 mL	3 mL	4 mL
Flu	12± 1	12± 1	11± 1
PhA	56± 3	55± 3	55± 3
AnT	58± 3	58± 3	58± 3
FluA	75± 3	75± 3	74± 3
Pyr	77± 3	77± 3	76± 3
BaA	74± 3	73± 3	73± 3
Chr	90± 4	90± 4	90± 4
BbF	87± 3	86± 3	86± 3
BkF	88± 4	87± 4	87± 3
BaP	98± 4	97± 4	97± 4
InP	97± 4	96± 4	96± 4
DbA	95± 4	94± 4	94± 4
BghiP	99± 4	98± 4	98± 4

Mean ± standard deviation values (n = 3). Bold values indicate the clean-up recovery obtained under the optimized conditions (elution: 2 mL of dichloromethane).

volume from 2 to 4 mL. The obtained R% data showed similar values for the different conditions, suggesting not significantly effect of the elution volume (Table 1). Therefore, the lowest volume of 2 mL was chosen for elution, in order to reduce solvent consumption and sample dilution.

In conclusion, under these optimized elution conditions, the MIP-SPE procedure provided excellent recovery of 95%–99% for BaP, InP, DbA and BghiP and close to 90% for Chr, BbF and BkF. However, the extraction yield decreased to ~ 75% for FluA, Pyr and BaA, and to ~ 57% for PhA and AnT (bold values in Table 1). Such results are consistent with the affinity of the tailored binding sites of the imprinted polymer (Krupadam et al., 2010; Ho et al., 2011; Sun et al., 2017).

In addition, the effect of the SPE operative conditions was investigated for C₁₇ - C₃₂ n-alkanes, by computing analyte recovery in dichloromethane eluate. Fig. 1b reports the measured recovery (mean and standard deviation values) after changing cyclohexane volume for cartridge conditioning (from 1 to 4 mL, left side) and washing (from 1 to 3 mL, right side) for C₁₉ - C₃₁ terms (lighter and heavier n-alkanes always yielded no recovery). All the results clearly showed that the target n-alkanes were nearly fully removed by the clean-up procedure, independent of the protocol used. In fact, under the optimized MIP-SPE conditions, only few series terms were left in the dichloromethane eluate at trace level, with R% ranging from 2% to 5%, i.e., C₂₁, C₂₃, C₂₅, C₂₇, C₃₀ and C₃₁.

2.2. Validation of the MIP-SPE clean-up procedure

The proposed MIP-SPE procedure was validated under the optimized conditions, by evaluating some figures of merit, such as the calibration linear range, limits of detection and quantitation, precision, accuracy and selectivity. The study was performed on the 10 heavier PAHs which showed good recovery (R% ≥ 75%), i.e., from FluA to BghiP. Standard solutions were prepared in cyclohexane at eight concentration levels between 1 and 300 ng/mL for each target PAH. These concen-

trations in sample solution (500 µL) correspond to 0.008 – 2.5 ng/m³ level in the ambient air, under the used sampling conditions and clean-up protocol.

Linearity and linear range of the method were obtained from analytical standard calibration curves detected in the SIM mode. Linear relationship was observed between the peak area and analyte concentration over the linear range of the calibration curve, with correlation coefficients above 0.991 (at the statistical significance level $p < 0.05$). The results for linearity, detection and quantification limits are presented in Table 2. The limits of detection (LOD) and quantitation (LOQ) were calculated as equal to a signal-to-noise ratio of three and ten times for LOD and LOQ, respectively. The LODs for the investigated PAHs ranged from 3.9 ng/mL (Chr) to 11.4 ng/mL (FluA) whilst the LOQs ranged from 13.5 (Chr) to 38.1 ng/mL (FluA) in the injected solution, corresponding to 0.03 to 0.09 ng/m³ and to 0.12 to 0.33 ng/m³ in the ambient air, respectively.

The comparison with literature data reveals that these LOQs, expressed as concentration in the injected solution, are similar to those obtained with other methods based on GC/MS analysis (Ballesteros et al., 2009; Ding et al., 2011; Cochran et al., 2012), but higher than those based on tandem GC/MS/MS (Nyiri et al., 2016; Kim et al., 2019; Naing et al., 2020). Overall, LODs are consistent with some literature data, if they are expressed in terms of ng/m³ concentration in the sampled air (Nyiri et al., 2016; Santos et al., 2016).

Repeatability was evaluated as intra-day precision from five replicate analyses of PAH standard solutions at the medium concentration level of 100 ng/mL (i.e., 0.8 ng/m³ in the sampled air). Overall, the method presented a good precision, as the relative standard deviations (RSD%) ranged between 2.5% and 5.9% for all of the investigated PAHs.

The method trueness was assessed by measuring the PAHs recovery on real PM_{2.5} samples spiked with known amount of PAHs. The study was performed on four urban PM_{2.5} samples (samples 1-4) analyzed in triplicate. After the solvent extraction, spiked samples were prepared by adding a standard working solution of 10 PAHs (from FluA to BghiP), each at concentration of 200 ng/mL (corresponding to an air concentration of 1.7 ng/m³ in the sampled air, under the operative conditions). The recovery (R%) of each target PAH was computed as the ratio between the peak area measured for the spiked filter and that for the standard solution used for spiking. Thus, the computed value included the clean-up recovery and the potential sample matrix effects (Table 3). An excellent recovery in the 90%–96% range was provided for the PAHs containing more than 4 aromatic rings, from BbF to BghiP, for which the MIP sorbent is specifically tailored (Krupadam et al., 2010; Ho et al., 2011; Sun et al., 2017). A slight decline to 85%–72% values was observed for PAHs containing more than 3 aromatic rings, from FluA to Chr. These values were very close to those measured from the PAH standard mixtures (Table 1), so proving the good performance of the optimized SPE procedure. However, it is noteworthy that such a benefit is limited to the heavier PAHs containing more than 4 benzene rings. Indeed, they consist of the highly carcinogenic dibenzopyrene isomers, including BaP (Krupadam et al., 2010; Ho et al., 2011; Sun et al., 2017). Overall, the above results revealed that the present method is acceptably accurate and reliable for the de-

Table 2 – Quantitative results of the MIP-SPE procedure of PAHs under optimized conditions: linearity (expressed as correlation coefficient R^2), sensitivity (expressed as slope of the calibration curve for the calibration range listed), limit of detection (LOD), limit of quantification (LOQ) and precision (RSD%, relative standard deviations from five replicate measurements).

PAH	Calibration range (ng/mL) ^a	R^2	Sensitivity	LOD (ng/mL)	LOD (ng/m ³)	LOQ (ng/mL)	LOQ (ng/m ³)	Intra-day RSD% ^b
FluA	35 - 300	0.995	7.9	11.4	0.09	38.1	0.33	3.6
Pyr	15 - 300	0.992	14.5	4.8	0.03	15.9	0.12	4.9
BaA	18 - 300	0.996	12.5	5.4	0.06	18.3	0.15	3.8
Chr	13 - 300	0.999	14.7	3.9	0.03	13.5	0.12	2.5
BbF	16 - 300	0.995	13.1	5.1	0.03	16.5	0.15	3.2
BkF	21 - 300	0.995	12.7	6.3	0.06	21.3	0.18	3.3
BaP	15 - 300	0.997	13	4.5	0.03	15.6	0.12	3.7
InP	25 - 300	0.992	8.1	7.5	0.06	25.2	0.21	4.6
DbA	24 - 300	0.998	6.7	7.5	0.06	24.6	0.21	5.7
BghiP	14 - 300	0.991	11.1	4.2	0.03	14.4	0.12	5.9

^a The range of calibration corresponds to the linear range. The lowest concentration corresponds to the LOQ value.

^b Calculated from standard solution containing 100 ng/mL of each PAH.

Table 3 – Percentage recovery of spiked PAHs in real PM_{2.5} samples.

PAHs	Sample 1	Sample 2	Sample 3	Sample 4	Mean ± S.D.
FluA	74	74	69	72	72 ± 2
Pyr	71	76	72	77	74 ± 3
BaA	72	74	78	76	75 ± 3
Chr	88	86	85	82	85 ± 3
BbF	93	89	92	90	91 ± 2
BkF	92	87	93	89	90 ± 3
BaP	97	93	92	96	95 ± 2
InP	93	95	98	96	96 ± 2
DbA	90	97	96	93	94 ± 3
BghiP	94	98	95	93	95 ± 2

termination of trace PAHs in ambient PM samples, retaining relevant information for assessing the carcinogenic risk associated to PAHs.

2.3. Comparison of MIP-SPE with SPME

A SPME procedure was also investigated in the study, in order to critically compare the advantages and disadvantages of the two methods in terms of effectiveness and selectivity for PAH clean-up and also reliability for analysis of real PM_{2.5} samples. A critical point is the choice of the fiber coating, as PAHs have different sorption behaviors on the fiber depending on their different physicochemical properties (Pawliszyn, 2000; Li et al., 2015; Naccarato and Tagarelli, 2019). To date, the bipolar PDMS/DVB and the relatively polar PA fibers are recommended as the most appropriate polymeric phases for the extraction of PAHs from various environmental matrices (Al-Alam et al., 2017; Resende dos Santos et al., 2019), including PM extracts (Ballesteros et al., 2009; Menezes and Cardeal, 2011; Santos et al., 2016; Naing et al., 2020). Therefore, such fibers were evaluated in this study, with the specific concern of the selective clean-up of PAHs towards *n*-alkanes. Methanol standard solutions were used, containing 16 PAHs and 16 *n*-alkanes (C₁₇ to C₃₂) at concentration of 25 ng/mL of each compound, which corresponds to the same concentration of 0.83

ng/m³ in the sampled air, as that used in the MIP-SPE optimization. The experiments were performed in triplicate by direct immersion of fibers in a 5 mL vial containing 2.0 mL of methanol solutions. The extraction and desorption conditions were held constant in all the experiments.

The effect of the SPME procedures was evaluated by measuring the chromatographic responses (peak areas) of each target analyte after purification on PDMS/DVB and PA fibers (Fig. 2). It can be seen that both fibers show similar extraction efficiency for PAHs, with higher values for PAHs containing 3 or more fused-benzene rings, which met the theory (Pawliszyn, 2000) and literature results (Ballesteros et al., 2009; Menezes et al., 2011; Naccarato et al., 2019; Naing et al., 2020). Otherwise, the PDMS/DVB coating showed higher extraction efficiency than PA for the investigated *n*-alkanes, with an increase of 4 times up to 9 times for C₃₀ and C₃₂ *n*-alkanes (black bars in Fig. 2). This is consistent with the literature data, as the fully apolar *n*-alkanes can strongly interact with the PDMS/DVB coating, but only very weakly with the polar PA fiber (Menezes et al., 2011; Al-Alam et al., 2017; Naccarato et al., 2019; Resende dos Santos et al., 2019; Naing et al., 2020). Overall, the obtained results showed that the more polar PA coating was able to selectively adsorb PAHs in comparison with *n*-alkanes. Thus, such a selectivity is the basis for choosing the PA fiber for separating PAHs from *n*-alkanes, which interfere the GC/MS signal of the complex PM samples. Therefore, the PA fiber was chosen herein for comparison with MIP-SPE.

Then, the enrichment factor (EF) of the SPME procedure was estimated, as a consequence of the solvent-less nature of the SPME injection. The study was performed in triplicate by direct immersion of the PA fiber in 2.0 mL of a standard methanol solution containing 16 PAHs at 25 ng/mL level. The enrichment factor was computed for each PAH as the ratio of the peak area of the SPME extracted analyte to the peak area of direct injection of the original methanol solution (mean and SD values reported in Table 4). As expected, the measured EFs increased with the number of the condensed rings and the hydrophobicity of the PAHs (Menezes and Cardeal, 2011; Li et al., 2015; Al-Alam et al., 2017; Resende dos Santos et al., 2019). Thus, the lighter PAHs are partially lost in comparison with

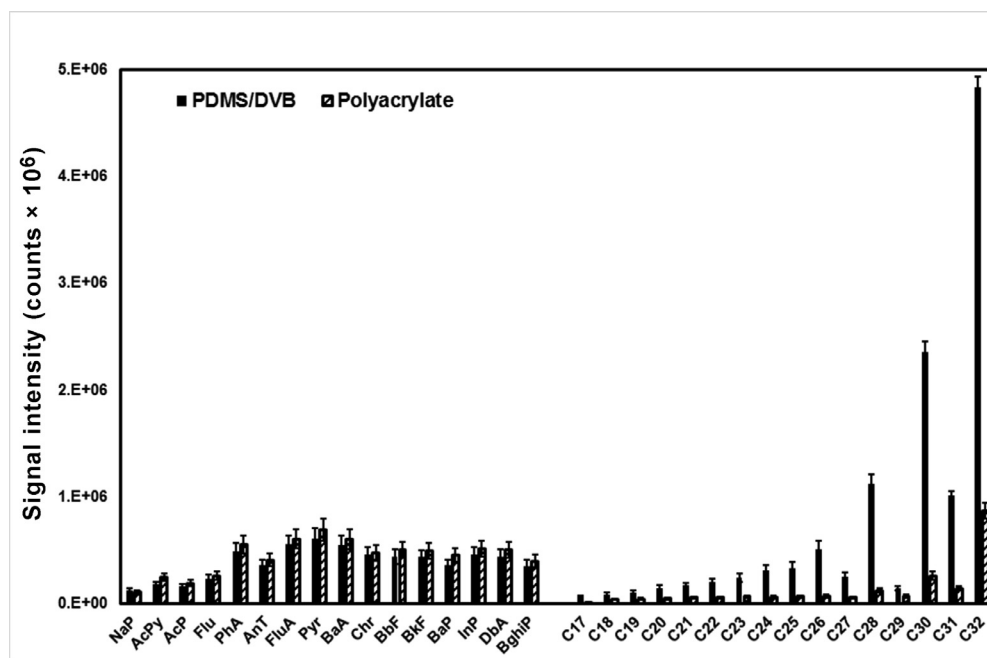


Fig. 2 – Effects of the SPME fiber coatings on the extraction efficiency: comparison between the signal intensity of standard mixtures of PAHs and C₁₇–C₃₂ n-alkanes (100 ng/mL in methanol) after clean-up on PDMS/DVB and PA fibers. Bars report mean and standard deviation values ($n = 3$).

Table 4 – Enrichment factor of SPME procedure on PA fiber for the investigated PAHs (methanol solution at 25 ng/mL)

Compound	Enrichment factor ^a
NaP	0.60±0.03
AcPy	0.64±0.04
AcP	0.55±0.03
Flu	0.74±0.04
PhA	0.91±0.05
AnT	0.92±0.05
FluA	1.18±0.07
Pyr	1.27±0.08
BaA	1.38±0.09
Chr	1.48±0.09
BbF	2.15±0.13
BkF	2.20±0.14
BaP	2.53±0.14
InP	2.55±0.16
DbA	2.62±0.15
BghiP	2.67±0.17

^a mean ± standard deviation from three replicate analyses.

the direct injection, while the heaviest PAHs are enriched up to a factor of 2.6. Such an enrichment is able to compensate the dilution of the SPME procedure into a solution volume of 2 mL, that is required to guarantee a full immersion of the SPME fiber, in comparison with the volume of 500 μ L in SPE method.

2.4. Application to PM_{2.5} real samples

The applicability of the MIP-SPE and SPME methods to real-world PM_{2.5} samples was comparatively investigated by ana-

lyzing six ambient PM_{2.5} filters collected at an urban site during winter 2017. High PAHs concentrations were expected in such samples, given the contribution of numerous emission sources present in the area, such as vehicle traffic, industrial activity and biomass combustion for residential heating in the cold season (Keith, 2015; Nozière et al., 2015; Abdel-Shafy and Mansour, 2016; Masala et al., 2016; Kim et al., 2019; Nyiri et al., 2016; Zhang et al., 2021). In addition, a large contribution of alkanes was expected, mainly n-alkanes with $C_{max} \leq C_{26}$ related to anthropogenic sources, in combination with series terms with $C_{max} > C_{26}$, which are typically emitted from biogenic sources, and several branched isomers, generating the unresolved carbon mixture (UCM) band in the GC/MS signal (Chan et al., 2013; Pietrogrande et al., 2014; Lyu et al., 2019; Wang et al., 2019; Naing et al., 2020).

The benefit of both clean-up procedures can be clearly depicted in Fig. 3a, which reports the comparison among the total ion chromatograms of a real PM_{2.5} filter (sample 1 in Table 2) without any clean-up (dashed black trace) and those after the MIP-SPE and SPME procedures (red and black tracers, respectively). The GC/MS signal of the untreated solution (dashed black trace) is very complex, mainly dominated by the unresolved alkane band and several overlapped peaks. In comparison, the chromatograms of the purified solutions are strongly simplified, since they are nearly lacking the alkane band. These plots clearly show the efficiency of the clean-up procedure in selectively retaining interfering hydrocarbons. Such a benefit is even more evident from a visual inspection of the SIM GC/MS signals at m/z values 57+71+85, which are mainly generated by the n-alkanes (Fig. 3b). In comparison with the original extract (dashed black trace), both purified solutions show a strong reduction of the hydrocarbons generating the unresolved band, so that most of the mixture

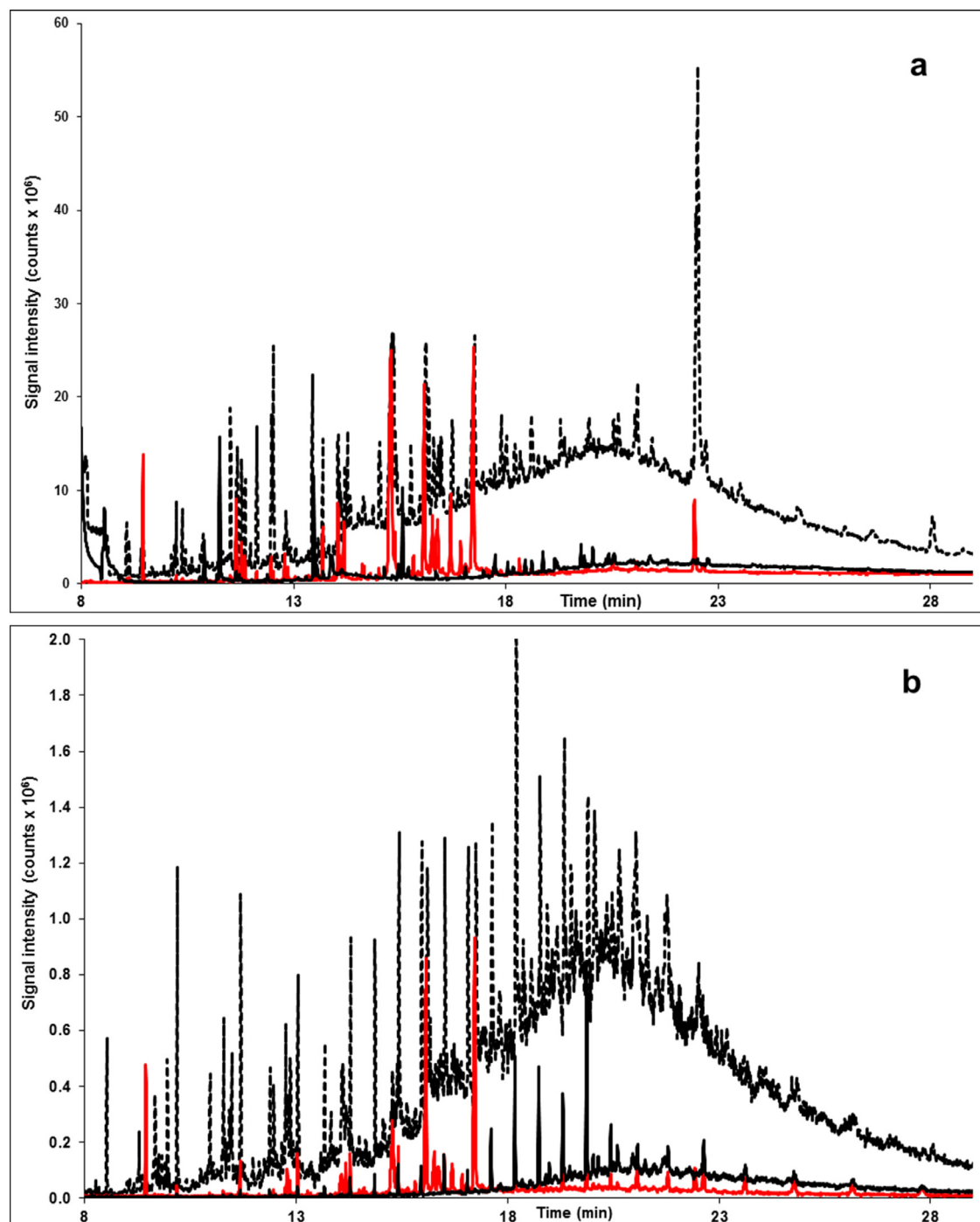


Fig. 3 – Effects of both clean-up procedures on the GC/MS chromatograms of a real PM_{2.5} filter (sample 1 in Table 2): comparison between the signals of the untreated solution (dashed black trace) and those of the purified solutions using the MIP-SPE (red trace) and SPME procedures (black trace). (a) signal intensity from total ion detection mode and (b) signal intensity from SIM detection mode at m/z values 57+71+85.

components can be properly separated and identified in the chromatograms (red and black traces, respectively). In addition, the two signals clearly show different complementary selectivity of the two clean-up procedures. The adsorption on the PA fiber can strongly reduce the UCM band, but it cannot remove the interfering hydrocarbons corresponding to C₂₇ - C₃₀ n-alkanes, which elute in the same 17-20 min retention

region, as 5 rings PAHs (black trace). On the contrary, the SPE on the MIP polymer is able to eliminate the heavier alkanes, so that the UCM components are nearly absent and only lighter C₂₁-C₂₅ n-alkanes are still present in the mixture (red trace). Thus, the MIP-SPE procedure appeared more efficient than SPME in removing hydrocarbons, which may interfere with heavier PAH signal.

Table 5 – % recovery of the SPE procedure for target PAHs in the real PM_{2.5} samples.

PAHs	PM-1	PM-2	PM-3	PM-4	PM-5	PM-6	Mean
FluA	65	66	69	71	68	66	68
Pyr	67	65	72	70	71	65	68
BaA	68	64	71	74	73	64	69
Chr	83	82	84	86	85	82	84
BbF	82	90	90	89	92	81	87
BkF	81	92	92	89	91	88	89
BaP	94	93	93	95	94	92	94
InP	91	92	94	96	93	92	93
DbA	94	93	95	94	95	92	94
BghiP	93	92	91	96	95	93	93

The target PAHs were quantified in the real samples, by submitting each original PM extract, prior to clean-up, to the GC analysis combined with tandem mass spectrometry detection (GC/MS/MS). The SRM conditions specific for each PAH were applied, as recovered from literature (Kim et al., 2019; Naing et al., 2020). Thus, the measured values can be assumed as the true PAH concentrations in the real samples, since they are accurate results obtained by tandem MS, as the most sensible and selective detection mode able to avoid interferences in the GC/MS signal (Nyiri et al., 2016; Kim et al., 2019; Naing et al., 2020). Most of the 16 target PAHs were identified and quantified in the study samples, with total concentrations ranging from 6.33 up to 11.94 ng/m³. Such values appear broadly consistent with those described in urban atmospheres in other Italian sites (Masiol et al., 2013; Pietrogrande et al., 2014) and also in Europe (Ramírez et al., 2010; Abdel-Shafy and Mansour, 2016; Masala et al., 2016; Nyiri et al., 2016; Alves et al., 2017; Kim et al., 2019). Concerning the distribution profiles of individual PAHs, we can observe a general concentration increase with molecular weight, dominated by four and five rings congeners - BaA, Chr, BbF, BkF, BaP, InD and BghiP -, as commonly seen in PAH datasets (Alves et al., 2017; Li et al., 2015; Niu et al., 2017). Among them, BbF, BkF, InP and BghiP were the most abundant (up to 1.20 ng/m³), that is consistent with the sampling urban location, since they have been associated with gasoline-powered vehicles (Abdel-Shafy et al., 2016; Masiol et al., 2013; Nozière et al., 2015).

Then, each portion of the real PM_{2.5} samples was submitted to both SPE or SPME procedures and the purified solution analyzed with GC/MS. The PAH recovery of the SPE or SPME procedures was evaluated by assuming the GC/MS/MS data as true concentration in the original PM sample. Tables 5 and 6 report the % recovery values of SPE and SPME procedures computed for each PAHs in the 1-6 PM samples.

Overall, both procedures provided PAH recoveries ranging from 73% to 138%, which indicate acceptable accuracy in environmental analysis. However, a detailed inspection of the data points out specific advantages and drawbacks of each of the two procedures. The MIP-SPE method shows acceptable accuracy with R% values above 82% for PAHs heavier than chrysene to achieve the best recovery (R%=93%) for PAHs with 5 and more benzene rings (Table 5). In contrast, the SPME shows a

Table 6 – % recovery of the SPME procedure of target PAHs in the real PM_{2.5} samples.

PAHs	PM-1	PM-2	PM-3	PM-4	PM-5	PM-6	Mean
NaP	75	81	81	82	79	83	80
AcPy	80	86	75	78	80	84	81
AcP	86	80	77	75	75	85	80
Flu	80	88	73	82	76	79	80
PhA	75	75	80	77	84	80	79
AnT	80	80	83	79	88	80	82
FluA	86	76	75	80	76	86	80
Pyr	80	87	82	79	78	80	81
BaA	81	79	77	83	81	81	80
Chr	80	86	79	75	81	80	80
BbF	82	82	74	80	87	75	80
BkF	86	87	81	81	79	73	81
BaP	115	110	114	80	75	84	96
InP	138	114	112	83	75	70	99
DbA	136	126	122	75	80	71	102
BghiP	131	111	128	80	74	73	100

Bold values: overestimated results in the most polluted samples.

homogeneous recovery for all the investigated PAHs, independent of PAH molecular weight, with a mean acceptable value close to 80% (Table 6). However, some heavier PAHs, i.e., BaP, InP, DbA and BghiP, showed R% values from 110 to 138% in the most polluted samples PM-1 to PM-3 (bold values in Table 6). Such overestimation errors may be due to the positive interference of C₂₇ - C₃₀ n-hydrocarbons, which co-elute with PAHs and generate the same m/z fragment ions in the MS spectra, as shown in the SIM GC/MS signals reported in Fig. 3b (black trace). In particular, specific attention should be paid to the overestimation of BaP, due to overlapping with C₂₉ n-alkane, as this PAH is commonly used as a reference for assessment of the carcinogenic risk associated with PAHs.

3. Conclusions

As a general conclusion, the reported results demonstrated the potential advantages of the MIP-SPE for sample clean-up for analysis of PAHs in airborne particles, although limited to PAHs with more than 4 benzene rings. In particular, the great specificity of the SPE procedure is based on the capability of the MIP sorbent of selective recognition binding with target PAHs. Thus, undesirable matrix interferences can be removed from the complex sample to improve the specificity and sensitivity of the MS ion-trap detector. This is the case of high levels of interfering hydrocarbons, commonly present on ambient PM strongly impacted by traffic emission. In contrast, SPE suffers the drawbacks of requiring pre-concentration by solvent evaporation of the extracted solutions, that increases the run time and can cause a decrease in analytical reproducibility.

The SPME procedure is a green alternative, since it reduces the number of steps by eliminating the use of solvents to avoid exposure risk and environmental contamination. The current work confirmed the good performance of the polyacrylate SPME fiber in extraction and purification of the PM-associated PAHs, with homogenous recovery for all the target PAHs, having the big benefit of a minimal number of steps.

However, the SPME clean-up can only partially remove heavy hydrocarbons from the PM extract, so that they can interfere in the SIM chromatographic signal of the 5 rings PAHs to generate quantification errors.

Based on the critical comparison between MIP-SPE and SPME methods, we can conclude that both procedures compare in terms of reliability, accuracy and sensibility for PAH analysis in PM samples, but the MIP-SPE exceeds in the specific selectivity towards hydrocarbons in PM, in particular towards the highly carcinogenic dibenzopyrene isomers. Thus, this is the procedure of choice for the preconcentration/separation of PAHs in urban polluted PM samples, although the disadvantages of requiring labor intensive and time-consuming sample pretreatment.

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