



Development and validation of a multi-pollutant method for the analysis of polycyclic aromatic hydrocarbons, synthetic musk compounds and plasticizers in atmospheric particulate matter (PM_{2.5})

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ABSTRACT

Exposure to atmospheric particulate matter (PM) associated pollutants is a global concern due to the risk posed in human health after inhalation. In this study, a simple and sensitive multi-residue method is developed for the analysis of 50 organic pollutants, comprising 18 polycyclic aromatic hydrocarbons (PAHs), 12 phthalate esters (PAEs), 12 organophosphorus flame retardants (OPFRs), 6 synthetic musk compounds (SMCs) and 2 bisphenols in PM_{2.5} samples. The method consists of three cycles of ultrasonic assisted solvent extraction and vortex (UASE + vortex), followed by a vortex-assisted dispersive solid phase extraction (d-SPE) clean-up and a final determination step by using programmed temperature vaporization-gas chromatography-tandem mass spectrometry (PTV-GC-MS/MS). Experimental conditions concerning clean-up adsorbents (alumina, silica gel and Florisil®) and filters (glass fibre, PTFE and nylon), as well as PTV-GC-MS/MS conditions were studied. In addition, the use of SRM (selected reaction monitoring) mode in MS-MS, as well as matrix-matched calibration together with labelled surrogate standards, resulted in successfully validation results for most of the compounds due to the high sensitivity, minimization of matrix effects and recovering losses compensation. The proposed method was validated in terms of linearity, limits of detection and quantification (LODs and LOQs), analytical recoveries by analysing a spiked composite sample (PM_{2.5}) at three spiking levels and intra-day and inter-day precision. Moreover, an urban particulate matter standard reference material (SRM 1648a) was analysed to assess PAHs determination accuracy. Furthermore, applicability of the method was proved by analysing 12 PM_{2.5} samples from an industrial area. Among all studied pollutants, bisphenol A (BPA) was the most predominant with an average concentration of 5000 pg m⁻³, followed by bis(2-ethylhexyl) phthalate (DEHP) and diisobutyl phthalate (DiBP) with 1990 pg m⁻³ and 632 pg m⁻³, respectively. Concerning OPFRs, average concentrations between 345 – 253 pg m⁻³ were found for triphenyl phosphine oxide (TPPO), tris(chloropropyl) phosphate (TCPP), tri-isobutyl phosphate (TiBP) and tris(2-butoxyethyl) phosphate (TBOEP). Finally, the highest PAHs levels were found for 5-6 ring-number PAHs (Σ₅₋₆ rings PAHs) with an average concentration of 2680 pg m⁻³, while only 2 SMCs were quantitated accounting for 17.5 pg m⁻³ by average.

1. Introduction

The release of pollutants to the atmosphere due to anthropogenic activity represents an important impact on air quality, driving global climate change and posing an important risk on human health [1], and being considered to be responsible of approximately 3 million deaths worldwide every year [2]. Among air pollutants, atmospheric

particulate matter (PM) was classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (Group 1) [3], being fine particulate matter (PM_{2.5}) the fraction that triggers the most relevant health problems [4–6]. Several adverse PM outcomes in human health (mainly related to respiratory and cardiovascular alterations and diseases) have been demonstrated by many studies [7–12], that are thought to be dependent on the PM-associated pollutants that could

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introduce in our body after inhalation [13–15]. Nevertheless, relationship between PM composition and toxicological and health effects are vaguely understood due to the spatiotemporal variability [14].

In the present study, special attention has been paid to polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PAEs), organophosphorus flame retardants (OPFRs), synthetic musk compounds (SMCs) and bisphenols because of their toxicity and ubiquity in the environment. Carcinogenic, mutagenic and immunosuppressant effects have been proved for several PAHs [16–18]; while neurotoxic, carcinogenic and adverse reproductive effects were associated to OPFRs [19–21] and SMCs exposure (as well as endocrine dysfunction) [22,23]. Furthermore, PAEs and bisphenols are considered endocrine disruptors, exhibiting similar health effects associated to reproductive developmental and neurological toxicity in humans [24–33]. PAHs are well-known air pollutants that are mainly emitted to the atmosphere as a result of incomplete combustion processes (e.g. biomass and fossil fuels) and their occurrence in atmospheric PM fractions (PM₁₀ and PM_{2.5}) has been studied in different areas by many researchers [34–39]. On the contrary, the occurrence in the environment of the remaining compounds (PAEs, OPFRs, SMCs and bisphenols) is primarily due to their wide application in many industries such as plastics, electronics, furniture and personal care [19,31,40,41], being many of them considered as high-production volume (HPV) chemicals by the USEPA [42].

Some extraction techniques such as solid-liquid extraction (SLE) [43–46]; pressurized liquid extraction (PLE) [39,47–49]; and ultrasonic assisted solvent extraction (UASE) [50–57], or UASE combined with vortex (UASE + vortex) [58–63], were frequently used for extracting the studied compounds from environmental solid matrixes. Among them, UASE + vortex was the most used methodology for all the compound families included in the present study, generally followed by solid-phase extraction (SPE) clean-up using alumina [48,64], Florisil® [58,63] and silica gel [65–67] commercial cartridges. However, dispersive solid-phase extraction (d-SPE) clean-up was reported to be an interesting methodology to perform extracts clean-up because of its fastness and simplicity [68]. This technique has been mainly applied by many researchers to analyse pesticides in plant origin foods [69,70] and other organic compounds in foods [71–73]. Furthermore, some studies have shown high clean-up efficiencies by using d-SPE in the analysis of PAHs in PM₁₀ [74] and secondary organic aerosol tracers in urban dust [75]. Regarding analysis of target compounds, gas chromatography coupled to mass spectrometry (GC-MS) [51,53–55,57–60,62] and gas chromatography-tandem mass spectrometry (GC-MS/MS) [52,58,61, 63] have been proved to be an efficient separation and determination techniques for compounds under study, providing high sensitivity and specificity in the analysis in the ultimate case. Moreover, the use of large-volume injectors such as a programmed temperature vaporization (PTV) injector allows the introduction of higher volumes of sample in comparison with other injector such as split/splitless, improving the sensitivity in GC analysis [76].

Within this context, a multi-residue methodology could provide a useful tool to achieve a better understanding the relationship between PM composition and health outcomes gap, as a multi-pollutant approach is considered to be more representative of what is present in real samples [63], as well as other advantages regarding reduction of costs, time, solvents and required sample. In this framework, it could be a valuable methodology to organic characterization of PM used in animal exposure testing, in order to study the possible relationships between PM components and specific effects that inhaled PM may trigger in localized organs such as recently conducted in mice brain tissue [77], as well as observed in lung and colon [78].

The main aim of this study is the development and validation of a novel and simple multi-residue analytical method to assess 51 organic pollutants in PM_{2.5} samples (comprising 19 PAHs, 12 PAEs, 12 OPFRs, 6 SMCs and 2 bisphenols) based on UASE + vortex extraction, d-SPE clean-up and subsequent analysis by PTV-GC-MS/MS. Although some multi-residue analytical methodologies have been found in the literature

related to simultaneous extraction and analysis of the studied compounds (comprising 14 PAHs, 6 OPFRs and BPA in indoor dust [63]; 16 PAHs, 9 OPFRs and 9 SMCs in sediments [48]; 18 PAHs, 11 OPFRs and bisphenol A (BPA) in soils and indoor dust [49]; and 6 OPFRs and 6 PAEs in PM_{2.5} samples [79]) to the best of our knowledge, the number of target compounds included in this study are higher than those found in literature, being this research one of the few multi-residue methodologies focused on atmospheric PM. Moreover, chromatography variables such as PTV and GC oven conditions and target compounds MS-MS transitions were studied, as well as some extraction parameters concerning clean-up adsorbents and filters. The validation of method was demonstrated by analysing a spiked composite PM_{2.5} sample and an urban particulate matter standard reference material (SRM 1648a) and applicability of the method was performed by analysing 12 PM_{2.5} samples from an industrial area of Vigo city (Northwest coast of Spain), in which compounds including all the pollutant families were found.

2. Materials and methods

2.1. Chemicals and solvents

Target compounds analysed in the present study comprising the 5 compounds families (PAHs, OPFRs, PAEs, SMCs and bisphenols), compounds used as surrogates (S) and internal standards (IS) are listed in Table 1, along with their short-names, CAS number and other data. Mixed standard solutions of solid reagents (OPFRs and bisphenols) were prepared in ethyl acetate by weighting individuals at 1000 µg mL⁻¹ level approximately, while for PAHs, PAEs and SMCs standards were prepared also in ethyl acetate by combining commercial solutions acquired (Table 1). All standard solutions were stored in amber glass vials in a fridge at 4 °C and sonicated for 2 minutes before using.

The solvents, ethyl acetate LiChrosolv® and hexane SupraSolv®, were both purchased by Merck-Millipore (Darmstadt, Germany), while Acetone Romil-SpS™ (Super Purity Solvent) was purchased from Romil (Cambridge, UK). Florisil® (60-100 mesh) used for the clean-up step was purchased from Sigma-Aldrich (St. Louis, MO, USA), which was cleaned by sonicating with hexane: acetone (1:1) during 1 h and activated at 130 °C overnight (approximately 12 h) before using [80]. Moreover, an eVol® XR digital analytical syringe (SGE, Melbourne, Australia) was used to avoid contamination derived from plastic pipette tips.

2.2. Sampling

Validation and applicability of the method was evaluated by analysing a composite PM_{2.5} sample and 12 PM_{2.5} samples collected from an industrial site of Vigo city (coordinates: 42°12'37.0"N 8°44'11.4"W) during the year 2017, respectively. Sampling and PM_{2.5} mass concentration determination were performed according to the European Norm 12341 (EN 12341:2015) [81], using quartz filters Ahlstrom Munksjö MK360 (Falun, Sweden) of 15 cm of diameter at 30 m³ h⁻¹ during 24 h. Before and after sampling, filters were conditioned at 20±1 °C and relative humidity of 50±5 % for 48 h, for mass determination by means of a microbalance. Moreover, several field blanks (blank filters left inside the sampler without collecting PM) were also collected (according to EN 12341:2015 [81]). Once mass concentration of PM_{2.5} was determined, filters were stored in a freezer (–18 °C) until further analysis.

2.3. Cleaning Procedure

To avoid organic contamination, glassware material was rinsed with acetone (EMSURE®, Merck Millipore, Germany) and cleared with ultrapure water (Milli-Q water purification system, Millipore, Bedford, MA, USA). Then, it was immersed inside an aqueous alkaline bath (Extran® MA 01, Merck-Millipore, Germany) and sonicated for 30 min (except for volumetric material, which was kept immersed for 48 h without sonication). Soapsuds were removed and rinsed using ultrapure

Table 1

Short name, CAS number (CAS #), molecular weight (M_w) and supplier of studied compounds, subrogates and internal standards (labelled as (S) and (PI), respectively), comprising all compound families (polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PAEs), organophosphorus flame retardants (OPFRs), synthetic musk compounds (SMCs) and bisphenols).

Compound	Short-name	CAS #	M_w (g mol ⁻¹)	Supplier
PAHs				
Acenaphthene ^a	Ace	83-32-9	154.2	SemiVolatile Calibration Mix #5 2000 µg mL ⁻¹ in methylene chloride, Restek Corporation (Bellefonte, PA, USA)
Acenaphthylene	Acy	208-96-8	152.3	
Anthracene ^a	Ant	120-12-7	178.2	
Benzo(a)anthracene	BaA	56-55-3	228.3	
Benzo(a)pyrene	BaP	50-32-8	252.3	
Benzo(b)fluoranthene	BbF	205-99-2	252.3	
Benzo(g,h,i)perylene	BghiP	191-24-2	276.3	
Benzo(k)fluoranthene	BkF	207-08-9	252.3	
Chrysene	Chry	218-01-9	228.3	
Dibenz(a,h)anthracene	DBahA	53-70-3	278.4	
Fluoranthene	Ft	206-44-0	202.3	
Fluorene	Fl	86-73-7	166.2	
Indeno(1,2,3-c,d)pyrene	IP	193-39-5	276.4	
Naphthalene ^a	Naph	91-20-3	128.2	
Phenanthrene	Phe	85-01-8	178.2	
Pyrene	Pyr	129-00-0	202.3	
Acenaphthylene d-8 (S)	Acy-d8	93951-97-4	160.3	PAH Surrogate Cocktail 200 µg mL ⁻¹ in methylene chloride (D2, 99.9%): methanol (D2, 99.9%) (50:50), Cambridge Isotope Laboratories, Inc. (Andover, MA, USA)
Benzo(a)pyrene d-12 (S)	BaP-d12	63466-71-7	264.3	
Benzo(ghi)perylene d-12 (S)	BghiP-d12	93951-66-7	288.3	
Fluoranthene d-10 (S)	Ft-d10	93951-69-0	212.3	
Naphthalene d-8 (S)	Naph-d8	1146-65-2	136.2	
Phenanthrene d-10 (S)	Phe-d10	1517-22-2	188.2	
Pyrene d-10 (S)	Pyr-d10	1718-52-1	212.3	
Anthracene d-10 (IS)	Ant-d10	1719-06-8	188.2	All compounds were purchased individually in 10 µg mL ⁻¹ standard solutions (except for BeP-d12, in 100 µg mL ⁻¹) in cyclohexane, Dr. Ehrenstorfer-LGC Standards (Augsburg, Germany)
Benzo(e)pyrene	BeP	192-97-2	252.3	
Benzo(e)pyrene d-12 (S)	BeP-d12	205440-82-0	264.3	
Benzo(j)fluoranthene	BjF	205-82-3	252.3	
Chrysene d-12 (S)	Chry-d12	1719-03-5	240.3	
Dibenzo(a,h)anthracene d-14 (IS)	DBahA-d14	13250-98-1	292.4	
Retene	Ret	483-65-8	234.3	
PAEs				
Butyl benzyl phthalate ^a	BBP	85-68-7	312.4	EPA Phthalate Esters Mix 2000 µg mL ⁻¹ in hexane, Sigma-Aldrich (Steinheim, Germany)
Bis(2-ethylhexyl) phthalate ^a	DEHP	117-81-7	390.6	
Di-n-butyl phthalate ^a	DBP	84-74-2	278.3	
Diethyl phthalate ^a	DEP	84-66-2	222.2	
Dimethyl phthalate ^a	DMP	131-11-3	194.2	
Di-n-octyl phthalate ^a	DOP	117-84-0	390.6	
Bis(2-methoxyethyl) phthalate	DMEP	117-82-8	282.3	1000 µg mL ⁻¹ standard solution in acetone, TechnoSpech (Barcelona, Spain)
Di-iso-butyl phthalate ^a	DiBP	84-69-5	278.3	
Di-iso-pentyl phthalate	DiPP	605-50-5	306.4	
Di-n-hexyl phthalate ^a	DnHP	84-75-3	334.6	
Di-n-pentyl phthalate	DNPP	131-18-0	306.4	
N-pentyl-isopentyl phthalate	NPiPP	776297-69-9	306.4	
Benzyl benzoate ^b (S)	BzB (S)	204-402-9	212.2	5000 µg mL ⁻¹ standard solution in hexane, Restek Corporation (Bellefonte, PA, USA)
OPFRs				
Tetraethyl ethylene diphosphonate	TEEdP	995-32-4	302.3	Solid 97 %, Sigma-Aldrich (Steinheim, Germany)
Triethyl phosphate d-15 (S)	TEP-d15	135942-11-9	197.2	Solid 99 %, CDN isotopes (Pont-Claire, Canada)
Tri-iso-butyl phosphate ^a	TiBP	126-71-6	266.3	Solid 95 %, Carbosynth Ltd (Compton, Berkshire, UK)
Tri-m-cresyl phosphate	TCrP	563-04-2	368.4	Solid 95 %, Sigma-Aldrich (Steinheim, Germany)
Tri-n-butyl phosphate ^a	TnBP	126-73-8	266.3	Solid 99 %, Sigma-Aldrich (Steinheim, Germany)
Tri-n-butyl phosphate d-27 (S)	TnBP-d27	61196-26-7	293.3	Solid 99 %, CDN isotopes (Pont-Claire, Canada)
Triphenyl phosphate ^a	TPhP	115-86-6	326.3	Solid 99 %, Sigma-Aldrich (Steinheim, Germany)
Triphenyl phosphate d-15 (S)	TPhP-d15	1173020-30-8	341.3	Solid 99 %, CDN isotopes (Pont-Claire, Canada)
Triphenyl phosphine oxide ^a	TPPO	791-28-6	278.3	Solid 99 %, Sigma-Aldrich (Steinheim, Germany)
Tripropyl phosphate	TPrP	513-08-6	224.2	Solid 99 %, Sigma-Aldrich (Steinheim, Germany)
Tris(2-butoxyethyl) phosphate ^a	TBOEP	78-51-3	398.5	Solid 94 %, Sigma-Aldrich (Steinheim, Germany)

(continued on next page)

Table 1 (continued)

Compound	Short-name	CAS #	M _w (g mol ⁻¹)	Supplier
Tris(1,3-dichloro-2-propyl) phosphate ^a	TDCPP	13674-87-8	430.9	Solid 99 %, Sigma-Aldrich (Steinheim, Germany)
Tris(2-chloroethyl) phosphate ^a	TCEP	115-96-8	285.5	Solid 97 %, Sigma-Aldrich (Steinheim, Germany)
Tris(2-ethylhexyl) phosphate ^a	TEHP	78-42-2	434.6	Solid 97 %, Sigma-Aldrich (Steinheim, Germany)
Tris(chloropropyl) phosphate, mixture of three isomers ^a	T CPP	13674-84-5	327.6	Solid 99 %, Sigma-Aldrich (Steinheim, Germany)
SMCs				
1-(6-(tert-Butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl) ethenone	Celestolide	13171-00-1	244.4	1000 µg mL ⁻¹ standard solution in methanol, TechnoSpech (Barcelona, Spain)
1,3,4,6,7,8-hexahydrocyclopenta[g]isochromene ^a	Galaxolide	1222-05-5	258.4	
2-(2-phenyl-imidazo[1,2-a]pyridin-3-yl)-ethylamine	Musk ketone	171346-87-5	237.3	
1,1,3,3,5-Pentamethyl-4,6-dinitroindane	Musk moskene	116-66-5	278.3	
1-tert-Butyl-3,5-dimethyl-2,4,6-trinitrobenzene ^a	Musk xylene	81-15-2	297.3	
6-Acetyl-1,1,2,4,4,7-hexamethyltetralin ^a	Tonalide	21145-77-7	258.4	
1-tert-Butyl-3,5-dimethyl-2,4,6-trinitrobenzene d-15	Muxk xylene-d15	877 119-10-3	312.4	Individually 100 µg mL ⁻¹ standard solutions in acetone, TechnoSpech (Barcelona, Spain)
6-Acetyl-1,1,2,4,4,7-hexamethyltetralin d-3	Tonalide-d3	1396967-82-0	261.1	
Bisphenols				
Bisphenol A ^a	BPA	80-05-7	228.3	Solid 99 %, Sigma-Aldrich (Steinheim, Germany)
Bisphenol A d-16 (S)	BPA-d16	96210-87-6	244.4	Solid 98 %, Dr. Ehrenstorfer-LGC Standards (Augsburg, Germany)
Bisphenol F	BPF	620-92-8	200.2	Solid 98%, Sigma-Aldrich (Steinheim, Germany)

^a Included in the USEPA's high production volume (HPV) chemicals [42].

^b BzB is frequently used as S or IS for phthalate compounds analysis (despite not being a phthalate)

water, and finally air-dried. Metallic material (such as spoon and filter puncher) was cleaned with acetone and ultrapure water respectively, and air-dried. All plasticware was avoided and manipulation was intended to be as minimal as possible to minimize blank signals of target compounds.

2.4. Extraction procedure

Six circular pieces of 1.6 cm² (12.1 cm²) of each PM_{2.5} samples (corresponding to a PM_{2.5} mass ranging between 0.18 – 2.4 mg) were placed into glass centrifuge tubes and spiked with 15 µL of surrogates mix in ethyl acetate, containing TEP-d15, Naph-d8, Acy-d8, TnBP-d27, BzB, Phe-d10, Musk xylene-d15, Tonalide-d3, Ft-d10, Pyr-d10, TPHP-d15, Chry-d12, BeP-d12, BaP-d12 and BghiP-d12 (1 µg mL⁻¹) and BPA-d16 (10 µg mL⁻¹), and left until the solvent was evaporated. After adding 20 mL of hexane: acetone (1:1), a sonication in an ultrasonic bath (J.P. Selecta, Barcelona, Spain) for 10 min followed by a vortex for 1 min (VXR basic Vibrax IKA, Staufen, Germany) were performed. This process was repeated 3 times without changing the extraction solvent. Once extraction was performed, extracts were centrifuged (Eppendorf 5804, Madrid, Spain) at 3000 rpm for 5 min. Then, the liquid phase was transferred to another glass centrifuge tube containing 1 g of Florisil® and approximately 5 mL of hexane: acetone (1:1) (solvent volume used to extraction tube cleaning) was added. Afterwards, a vortex (around 1400 rpm) for 5 min and centrifugation again at 3000 rpm for 5 min were performed and the liquid phase was filtered through nylon CLARIFY syringe filters™ (0.2 µm, 25 mm diameter) (Phenomenex, Torrance, CA, USA) to a 50 mL round-bottom flask (5 mL of hexane: acetone (1:1) were used to clean tubes and syringe). Cleaned up extracts were evaporated by using a rotary evaporator (35 °C and 475 mbar) to approximately 0.5 mL and carried to dryness by using a gentle N₂ stream. Finally, residues were reconstituted (sonicating for 3 min) with 300 µL of ethyl acetate containing internal standards (Ant-d10 and

DBaA-d14, 100 µg L⁻¹) and stored in a fridge at 4 °C until further analysis.

2.6. Apparatus and chromatographic conditions using PTV-GC-MS/MS

The chromatographic system consisted of a Thermo Finnigan (Waltham, MA, USA) Trace GC chromatograph equipped with Triplus auto-sampler, PTV (programmed temperature vaporiser) injector and triple quadrupole mass spectrometer (TSQ Quantum XLS). Target compounds separation was achieved using a DB-XLB column (60 m × 0.25 mm, 0.25 µm film thickness) (J&W Scientific, Folsom, CA, USA). An empty PTV Silcosteel® liner, with 2 mm of inner diameter purchased from Thermo Finnigan (Waltham, MA, USA) was also used. Helium (99.9999 %) was used as a carrier gas under a constant flow rate of 1.2 mL min⁻¹ and Argon (99.9992 %) was used as collision gas in SRM (selected reaction monitoring) mode.

Sample injection volume was 8 µL and the injector program was PTV splitless mode with 30 mL min⁻¹ split flow and 3 min of splitless time. The program started at 80 °C and heated at 1 °C s⁻¹ until 300 °C (held for 5 min) for the sample transfer phase. Then, temperature was risen to 320 °C during 14.5 min and held for 12.5 min with a flow of 70 mL min⁻¹ during the cleaning phase. GC oven temperature program started at 80 °C (held for 3 min), increased by 40 °C min⁻¹ to 110 °C (held for 2 min) and subsequently increased by 5 °C min⁻¹ to 170 °C. Then, an increase to 200 °C by 2.5 °C min⁻¹ (held for 3 min) and finally to 310 °C by 3 °C min⁻¹ (held for 15 min) were performed. The run lasts approximately 83 min (Figure S1).

The mass spectrometer operated in SRM mode, in which an ion of a particular mass (parent ion) is selected in the first quadrupole (electron impact ionization (EI) at 70 eV) of the MS and a product ion (derived from a fragmentation reaction of the precursor ion through collision energy (CE)) is selected in the final quadrupole analyser. The transfer line and ion source temperatures were set on 300 °C and 250 °C,

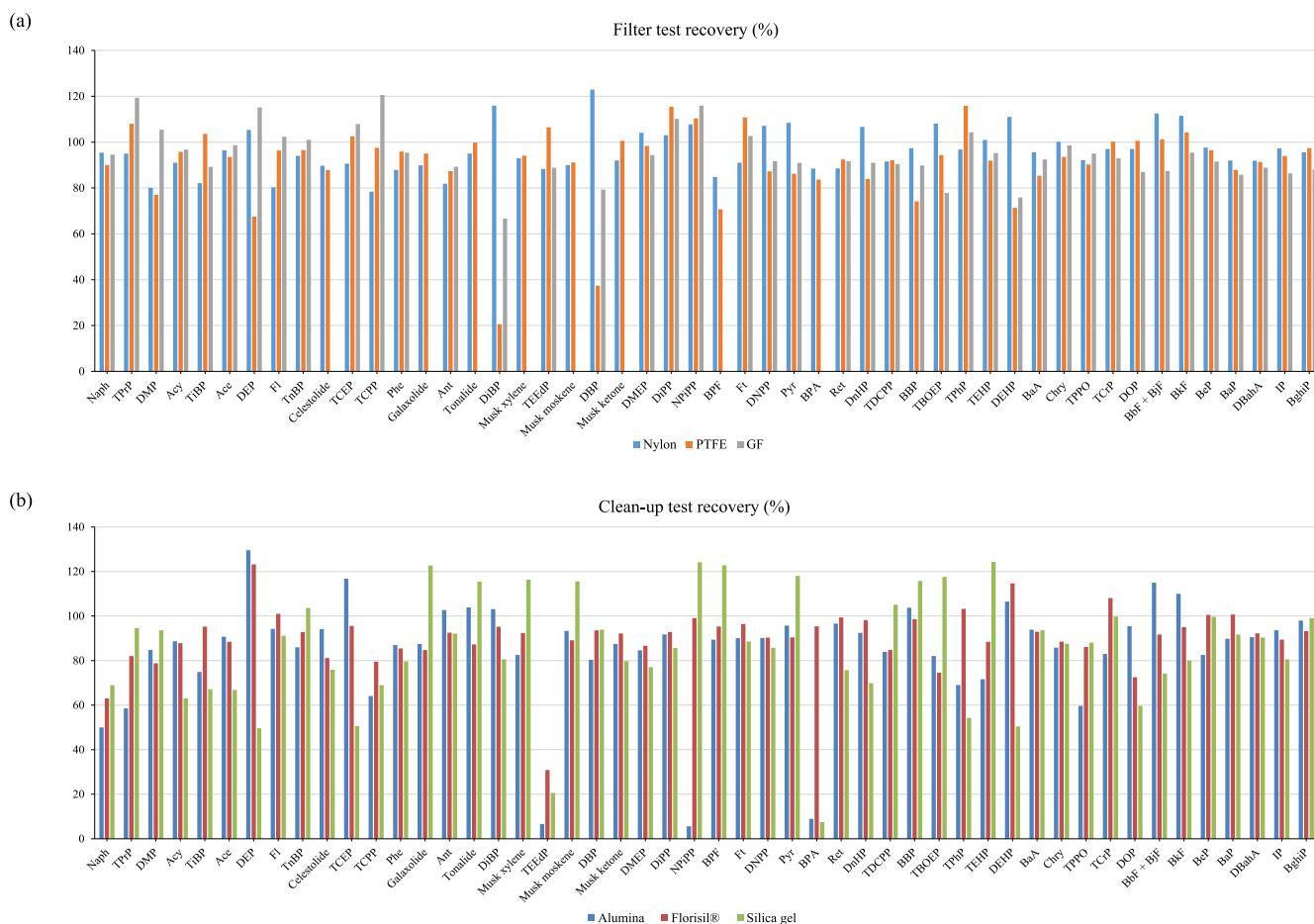


Fig. 1. Recoveries obtained for each target compounds in the filter (a) and clean-up adsorbent (b) testing.

respectively. Chromatograms in full scan and SRM mode obtained for a standard are shown in Figure S2.

2.7. Quantification and quality control

At least one procedural blank (commercial blank filter) and one field blank were analysed in each sample set to control possible contamination. Moreover, the average of field blanks was subtracted from the values obtained for samples because of being representative of sample manipulation (during sampling and analysis in the laboratory). Quantification was performed by using Xcalibur 2.1 (Thermo Finnigan, Waltham, MA, USA) as processor data. Control of the complete analytical procedure concerning the extraction step and chromatographic analysis was performed by means of surrogate compounds recoveries. Recoveries were calculated using relative response factors (RRFs) of surrogates with respect to internal standards. Retention times, quantification (Q) and confirmation (C) MS-MS transitions used, average RRFs and their RSDs, as well as internal standards used for each surrogate are shown in Table S1. Acceptable surrogates recoveries were considered to be within the range of 50 – 120 % basing on EN 15549:2008 [82], checking peaks integration or repeating the extraction if required.

3. Results and discussion

3.1. Target compounds extraction and clean-up conditions

Target compound extraction from PM_{2.5} samples was assessed following the UASE + vortex method described by Cristale and Lacorte et al. [58] (for polybrominated diphenyl ethers PBDE and OPFRs

extraction from sediment, sludge and indoor dust) and by Velázquez-Gómez et al. [63] (for PAHs, OPFRs and BPA extraction from indoor dust) with some modifications. After three cycles of 10 min sonicating + 1 min of vortex using 20 mL of hexane: acetone (1:1), different filters and d-SPE clean-up adsorbents were tested by using spiked and un-spiked extracts. All experiments were conducted in duplicates at 200 µg L⁻¹ level for target compounds, using all surrogates as IS (without using RRFs). Matrix-matched standards were also used to calculate recoveries and minimize matrix effects.

3.1.1. Filter testing

Two syringe filters comprising nylon (see Section 2.4) and PTFE (13 mm x 0.45 µm, Phenomenex, Torrance, CA, USA), as well as glass fibre filter papers (MN GF-6 φ=55 mm 0.6 µm Macherey-Nagel, Düren, Germany) (GF) were evaluated in terms of average recoveries and blank signals. Fig. 1a shows the recoveries obtained for each compound. Attending to the families averaged recoveries, nylon, PTFE and GF filters shown high recoveries for PAHs (95 %, 95 % and 93 % for nylon, PTFE and GF filters, respectively), OPFRs (93 %, 99 % and 99 % for nylon, PTFE and GF filters, respectively), and PAEs (104 %, 79 % and 94 % for nylon, PTFE and GF filters, respectively). Regarding bisphenols, mean recoveries of 87 % and 77 % were achieved when nylon and PTFE filters were used, respectively. Nevertheless, bisphenols were observed to be affected by GF matrix in the chromatographic system, that was translated in shifted and wider peaks (with respect to their retention time and peak shape without filtering) (Fig. S3). Then, GF filters were discarded for the analysis of the studied compounds. GF filters were not tested for SMCs due to the problem detected for bisphenols, showing averaged recoveries of 92 % and 95 % for nylon and PTFE filters, respectively

Table 2

Retention time (R_t); optimum MS-MS quantification (Q) and confirmation (C) transitions, both with their corresponding collision energy expressed in V (CE, V); internal calibration graphs ($y = bx + a$); correlation coefficients (R²); calibration ranges ($\mu\text{g L}^{-1}$); number of data points; surrogates (S) or internal standards (IS) used for the graphs and RRFs calculation; relative response factors (RRF); RRF relative standard deviations (RSD_{RRF}, %); and matrix effect coefficients (MEC) obtained for each compound considered in the present study.

Compound	R _t (min)	Q (CE, V)	C (CE, V)	Internal calibration graph ($y = bx + a$)	R ²	Calibration range ($\mu\text{g L}^{-1}$)	N ^o of data points	S or IS	RRF ^b	RSD _{RRF} (%)	MEC (%) ^d
Naph	13.5	128 → 102 (10)	128 → 77 (30)	$y = 0.0546x + 0.7014$	0.9978	0–500	9	Naph-d10	3.42	5.70	68
TPrP	17.8	183 → 99 (10)	99 → 63 (30)	$y = 0.0317x + 0.0158$	0.9998	0–640	9	Acy-d8	1.55	5.17	49
DMP	20.5	163 → 133 (10)	163 → 77 (20)	$y = 0.0233x + 0.0548$	0.9997	0–300	8	TnBP-d27	1.24	7.92	–3
Acy	21.1	152 → 74 (50)	152 → 126 (30)	$y = 0.0111x - 0.0275$	0.9995	0–300	8	Acy-d8	0.53	6.00	10
TiBP	21.2	99 → 63 (30)	112 → 82 (15)	$y = 0.0224x - 0.0281$	0.9998	0–340	8	TnBP-d27	1.08	4.47	31
Ace	22.1	153 → 151 (30)	153 → 126 (40)	$y = 0.0171x - 0.0334$	0.9994	0–300	8	Acy-d8	0.80	8.57	21
DEP	24.5	149 → 65 (20)	149 → 121 (10)	$y = 0.1069x - 0.7435$	0.9967	5–300	7	BzB	4.63	13.07	–1
Fl	25.6	166 → 165 (20)	166 → 139 (40)	$y = 0.1641x - 0.7274$	0.9993	0–300	8	Acy-d8	7.28	10.75	18
TnBP	25.7	211 → 99 (10)	155 → 99 (5)	$y = 0.0125x - 0.0938$	0.9991	0–580	9	TnBP-d27	0.54	10.00	–26
Celestolide	28.3	244 → 229 (10)	229 → 173 (8)	$y = 0.0310x - 0.0986$	0.9996	0–300	8	Tonalide-d3	1.37	7.57	18
TCEP	31.1	249 → 125 (10)	205 → 143 (5)	$y = 0.0213x - 0.0102$	0.9997	0–550	8	BzB	1.09	11.95	–18
TCPP	31.9 - 33.0	201 → 125 (5)	125 → 99 (15)	$y = 0.0094x + 0.0314$	0.9992	0–755	9	Phe-d10	0.52	9.11	13
Phe	33.2	178 → 152 (20)	178 → 151 (30)	$y = 0.0278x - 0.0587$	0.9995	0–500	9	Phe-d10	1.30	7.60	1
Galaxolide	33.5	243 → 213 (10)	258 → 243 (10)	$y = 0.4540x + 0.8961$	0.9997	0–500	9	Musk xylene-d15	23.32	7.66	–29
Ant	33.8	178 → 151 (30)	178 → 152 (20)	$y = 0.0113x + 0.0201$	0.9998	0–500	9	Phe-d10	0.57	7.22	–5
Tonalide	34.0	243 → 187 (8)	258 → 243 (10)	$y = 0.0197x - 0.0593$	0.9993	0–500	9	Tonalide-d3	0.89	7.64	40
DiBP ^a	34.1	149 → 65 (25)	149 → 121 (15)	$y = 0.0244x + 0.0711$	0.9976	0–500	8	Ant-d10	– ^c	– ^c	– ^e
Musk xylene	34.4	297 → 282 (10)	282 → 91 (30)	$y = 0.0100x + 0.0470$	0.9988	0–500	9	Musk xylene-d15	0.54	10.78	–39
TEEDP	34.4	137 → 109 (10)	257 → 173 (20)	$y = 0.0081x - 0.0323$	0.9993	2–445	8	Phe-d10	0.38	10.71	– ^f
Musk moskene	35.6	263 → 221 (8)	263 → 172 (15)	$y = 0.0555x + 0.0566$	0.9996	0–500	9	Musk xylene-d15	2.89	13.46	–63
DBP ^a	38.1	149 → 65 (25)	149 → 121 (15)	$y = 0.0121x + 0.0797$	0.9995	0–500	9	Ant-d10	– ^c	– ^c	– ^e
Musk ketone	39.4	279 → 118 (20)	279 → 191 (10)	$y = 0.0389x + 0.0920$	0.9956	0–500	9	Musk xylene-d15	1.91	6.16	–48
DMEP	40.0	104 → 76 (10)	149 → 65 (25)	$y = 0.0231x - 0.0771$	0.9996	0–500	9	Tonalide-d3	1.01	8.20	–100
DiPP	42.1	149 → 65 (25)	237 → 149 (10)	$y = 0.0897x + 0.0270$	0.9997	0–500	9	Tonalide-d3	4.56	6.19	–40
NPiPP	43.6	149 → 65 (25)	149 → 121 (15)	$y = 0.0575x + 0.0078$	0.9999	0–500	9	Tonalide-d3	2.89	5.14	–74
BPF	43.4	200 → 107 (10)	107 → 77 (15)	$y = 0.0028x - 0.0016$	0.9994	5–1010	8	BPA-d16	1.31	12.19	21
Ft	44.5	202 → 152 (30)	202 → 200 (40)	$y = 0.0050x - 0.0166$	0.9991	0–500	9	Chry-d12	0.22	9.25	–19
DNPP	45.1	149 → 121 (15)	149 → 65 (25)	$y = 0.0495x - 0.0552$	0.9994	0–500	9	Pyr-d10	2.41	6.82	–17
Pyr	46.6	202 → 152 (30)	202 → 200 (40)	$y = 0.0032x + -0.0089$	0.9993	0–500	9	Pyr-d10	0.15	7.05	–78
BPA	47.0	213 → 119 (15)	228 → 213 (10)	$y = 0.0052x + 0.0198$	0.9983	5–1060	8	BPA-d16	2.47	13.24	32
Ret	49.0	219 → 202 (40)	219 → 203 (20)	$y = 0.0131x - 0.0659$	0.9984	0–500	9	Chry-d12	0.57	11.17	–20
DnHP	51.2	149 → 65 (25)	149 → 121 (15)	$y = 0.1361x + -0.7987$	0.9985	0–500	9	TPhP-d15	5.81	10.71	–6
TDCPP	51.9	209 → 99 (10)	99 → 81 (20)	$y = 0.0200x - 0.1905$	0.9942	0–515	9	TPhP-d15	0.82	12.44	–84
BBP	52.0	206 → 149 (10)	149 → 65 (25)	$y = 0.0142x + 0.0093$	0.9994	0–500	9	TPhP-d15	0.71	9.73	47
TBOEP	52.9	125 → 99 (10)	153 → 125 (10)	$y = 0.0105x - 0.0573$	0.9958	0–730	9	TPhP-d15	0.42	12.64	–100

(continued on next page)

Table 2 (continued)

Compound	Rt (min)	Q (CE, V)	C (CE, V)	Internal calibration graph ($y = bx + a$)	R ²	Calibration range ($\mu\text{g L}^{-1}$)	N ^o of data points	S or IS	RRF ^b	RSD _{RRF} (%)	MEC (%) ^f
TPhP	53.5	215 → 168 (15)	325 → 169 (20)	$y = 0.0100x - 0.0113$	0.9998	0–560	9	TPhP-d15	0.49	8.30	35
TEHP	53.8	99 → 81 (20)	113 → 57 (10)	$y = 0.0427x - 0.3272$	0.9993	0–575	9	TPhP-d15	1.81	12.59	29
DEHP ^a	56.6	167 → 149 (5)	149 → 65 (25)	$y = 0.0331x - 0.0767$	0.9946	0–500	8	Ant-d10	– ^c	– ^c	– ^e
BaA	57.3	228 → 226 (30)	228 → 202 (30)	$y = 0.0422x - 0.1173$	0.9991	0–500	9	Chry-d12	2.00	7.77	–52
Chry	57.6	228 → 226 (30)	228 → 202 (30)	$y = 0.0431x - 0.1198$	0.9992	0–500	9	Chry-d12	2.04	7.32	–34
TPPO	57.7	277 → 199 (20)	278 → 199 (25)	$y = 0.0587x - 0.0436$	0.9995	0–520	9	TPhP-d15	2.97	7.99	42
TCrP	60.3	261 → 243 (10)	367 → 197 (20)	$y = 0.0097x + 0.0333$	0.9997	0–975	9	TPhP-d15	0.531	6.88	38
DOP	61.8	279 → 149 (10)	149 → 65 (25)	$y = 0.0111x - 0.0230$	0.9997	0–500	8	BeP-d12	0.53	7.65	–65
BbF + BjF	66.0	252 → 226 (30)	252 → 250 (30)	$y = 0.0055x - 0.0307$	0.9993	0–1000	9	BaP-d12	0.25	10.83	–38
BkF	66.2	252 → 250 (30)	252 → 226 (30)	$y = 0.0310x - 0.0912$	0.9995	0–500	9	BaP-d12	1.47	9.44	–37
BeP	67.9	252 → 250 (40)	252 → 226 (30)	$y = 0.0440x + 0.1332$	0.9993	0–500	9	BeP-d12	2.32	9.54	–15
BaP	68.4	252 → 250 (40)	252 → 226 (30)	$y = 0.0278x + 0.0953$	0.9990	0–500	9	BaP-d12	1.47	6.99	18
DBahA	77.2	278 → 252 (30)	278 → 250 (70)	$y = 0.0293x - 0.0291$	0.9992	0–500	9	BghiP-d12	1.40	6.03	–28
IP	77.2	276 → 274 (40)	276 → 272 (70)	$y = 0.4552x - 1.8396$	0.9989	0–500	9	BghiP-d12	20.60	5.81	–36
BghiP	79.8	276 → 274 (40)	276 → 272 (70)	$y = 0.3708x - 0.3831$	0.9995	0–500	9	BghiP-d12	18.10	3.93	–34

^a Solvent-based standards (without matrix) were used.

^b Relative response factors (RRFs) were calculated as the average of all calibration points within the linear range, after using the following equation for each one: $\text{RRF} = \frac{\text{Area}_{\text{compound}} \times \text{Concentration}_{\text{standard}}}{\text{Area}_{\text{standard}} \times \text{Concentration}_{\text{compound}}}$

^c Not calculated due to the high RSDs obtained (>20 %).

^d Matrix effect coefficients (MEC, %) were calculated according to Kmellár et al. [85] using the following equation: $\text{MEC}(\%) = \left(1 - \frac{\text{slope matrix}}{\text{slope solvent}}\right) \times 100$; where slope matrix and slope solvent corresponds with the internal calibration slope obtained using matrix-matched standards and solvent standards, respectively.

^e Not calculated due to the high presence in filters.

^f MEC corresponding to TEEDP was not calculated because only 3 points could be considered for solvent-based calibration graphs.

(Fig. 1a).

Concerning blank signals, similar results were obtained for all the filters tested with some exceptions (Fig. S4). In addition, considering all the studied compounds, PTFE and GF were observed to provide 57 % and 22 % more blank signals than nylon, respectively. Attending to the results obtained, nylon filters were selected because of showing a mean recovery of 95 % (considering all the studied compounds) with respect to PTFE (87 %), although both could be used for the analysis of the studied compounds.

3.1.2. Clean-up adsorbent testing by d-SPE

Three adsorbents comprising activated neutral alumina (Brockmann Activity I), Florisil® (60–100 mesh) and silica gel (for column chromatography), both purchased from Sigma-Aldrich (St. Louis, MO, USA) were evaluated for extracts cleaning-up. Experiments were performed by using 1 g of adsorbent and keeping a vortex for 5 min, basing on previous experience. Furthermore, adsorbents were previously cleaned with hexane: acetone (1:1) by sonicating for 1 h. Then, alumina was activated at 400 °C for 16 h [83], while silica gel and Florisil® were activated at 130 °C for 16 h [84] and 12 h [80], respectively.

Attending to the results shown in Fig. 1b, any of the sorbents tested could be used in the analysis of PAHs (93 %, 88 % and 94 % for Florisil®, silica gel and alumina, respectively), OPFRs (90 %, 88 % and 79 % for Florisil®, silica gel and alumina, respectively), PAEs (92 %, 85 % and 92 % for Florisil®, silica gel and alumina, respectively) and SMCs (89 %, 104 % and 91 % for Florisil®, silica gel and alumina respectively).

However, low recoveries were obtained for BPF (6 %) when using alumina and for BPA (9 % and 7 %) when using alumina and silica gel (Fig. 1b). Considering all the compounds, average recoveries were 92 %, 86 % and 73 % for Florisil®, silica gel and alumina, respectively. Therefore, Florisil® was selected for using in the clean-up step because of showing the best results for all the compounds under study.

3.2. Study of PTV and GC oven conditions

In order to set the best PTV conditions, it is necessary to study the variables that might affect solvent elimination efficiency during the injection. In the present study, a PTV splitless injection were selected basing on previous experience [76] and a brief univariate study were performed attending to the baseline and peak shape of target compounds, particularly for the most volatiles (TEP-d15, Naph-d8, Naph, TPrP, DMP, Acy-d8, TiBP and Ace) that were observed to be the most affected by PTV conditions. Injector initial temperature (T_{in}), split flow (mL min^{-1}) and initial oven temperature (T_{oven}) were the variables tested subsequently (basing on previous experiments). Attending to Fig. S5a, a T_{in} of 80 °C (split flow set in 30 mL min^{-1} and a T_{oven} of 70 °C) was selected due to be the one that gave the less baseline and less tailed peaks that might be attributed to a better solvent elimination. Once T_{in} was set, split flows of 10, 30 and 50 mL min^{-1} were tested to vent the solvent suitably (T_{oven} set in 70 °C). As Fig. S5b shows, chromatographic profiles obtained were similar for all split flows tested. However, split flows of 50 mL min^{-1} is observed to affect Naph peak height, obtaining a

Table 3

LODs and LOQs, analytical recoveries (n=6), intra-day (n=3) and inter-day (n=6) precision and estimated expanded uncertainty (U_{exp}) (n=6).

Compound	LOD ($\mu\text{g m}^{-3}$) ^a	LOQ ($\mu\text{g m}^{-3}$) ^a	Analytical Recovery \pm SD ^b (%)			Precision RSD ^d (%)		U_{exp} ^d (%)
			Low	Medium	High	Intra-day	Inter-day	
PAHs								
Acy	4.5	8.7	94 \pm 5	102 \pm 11	107 \pm 12	7.8	11.0	15
Ace	10.6	18.8	106 \pm 10	101 \pm 11	108 \pm 8	6.3	10.7	14
Fl	39.7	70.1	– ^c	107 \pm 26	116 \pm 12	9.8	18.0	35
Phe	18.8	27.9	– ^c	100 \pm 15	104 \pm 3	4.9	15.0	17
Ant	12.1	22.1	116 \pm 17	99 \pm 8	98 \pm 2	4.0	8.2	13
Ft	8.5	19.8	– ^c	83 \pm 9	89 \pm 3	7.5	10.6	36
Pyr	19.7	33.8	– ^c	107 \pm 5	108 \pm 3	4.3	4.7	17
Ret	14.9	38.2	– ^c	88 \pm 8	103 \pm 7	5.3	8.9	28
BaA	1.8	2.9	– ^c	105 \pm 11	98 \pm 5	1.7	10.6	17
Chry	1.3	2.5	– ^c	104 \pm 10	96 \pm 2	4.6	9.7	15
BbF + BbF	3.8	7.9	– ^c	113 \pm 9	100 \pm 5	5.7	7.6	19
BkF	2.4	5.4	– ^c	101 \pm 3	92 \pm 8	8.1	8.9	11
BeP	0.69	1.2	– ^c	99 \pm 15	100 \pm 10	12.8	15.1	21
BaP	1.1	2.0	– ^c	101 \pm 13	102 \pm 12	8.5	12.9	17
DBahA	3.5	7.5	85 \pm 8	105 \pm 15	118 \pm 2	5.1	14.2	19
IP	3.0	5.9	– ^c	112 \pm 10	115 \pm 3	2.2	8.7	29
BghiP	2.3	4.3	– ^c	101 \pm 4	101 \pm 4	3.8	4.1	12
PAEs								
DMP	19.8	34.3	– ^c	88 \pm 7	104 \pm 14	5.2	9.5	27
DEP	303	525	– ^c	– ^c	64 \pm 10	14.0	15.4	75
DiBP	618	887	– ^c	– ^c	106 \pm 20	16.3	19.2	25
DBP	1130	1790	– ^c	– ^c	96 \pm 21	12.9	21.6	29
DMEP	26.6	61.4	95 \pm 14	115 \pm 4	106 \pm 8	6.5	7.2	18
DiPP	35.0	67.1	– ^c	89 \pm 13	100 \pm 6	5.2	14.5	28
NPiPP	3.5	6.9	– ^c	103 \pm 25	122 \pm 3	5.0	23.8	24
DNPP	4.1	6.7	– ^c	57 \pm 8	88 \pm 9	8.3	10.7	29
DnHP	2.7	5.5	– ^c	94 \pm 16	94 \pm 3	4.6	16.7	21
BBP	20.6	41.8	– ^c	– ^c	50 \pm 17	32.8	34.7	104
DEHP	455	694	– ^c	– ^c	95 \pm 12	12.1	13.0	19
DOP	2.8	4.6	– ^c	95 \pm 9	100 \pm 11	9.7	9.4	17
OPFRs								
TPrP	24.3	47.3	– ^c	96 \pm 22	110 \pm 15	0.71	16.4	27
TiBP	20.6	38.0	– ^c	– ^c	108 \pm 19	12.9	18.1	26
TnBP	163	299	– ^c	107 \pm 28	96 \pm 10	9.6	10.2	17
TCEP	6.3	10.4	– ^c	48 \pm 6	64 \pm 4	5.5	5.8	74
TCPP	35.4	81.8	– ^c	78 \pm 11	80 \pm 4	8.8	11.0	43
TEEdP	43.4	76.2	– ^c	37 \pm 5	37 \pm 2	12.3	12.7	127
TDCPP	2.8	5.2	– ^c	111 \pm 11	109 \pm 5	4.6	4.8	22
TBOEP	28.5	61.2	– ^c	135 \pm 7	127 \pm 6	1.7	5.1	55
TPhP	9.0	21.1	– ^c	86 \pm 10	86 \pm 15	10.3	11.3	31
TEHP	14.5	36.7	– ^c	86 \pm 17	85 \pm 8	7.5	20.0	36
TPPO	50.5	98.4	– ^c	69 \pm 5	70 \pm 9	0.48	7.4	63
TCrP	3.0	6.6	109 \pm 4	90 \pm 6	92 \pm 8	4.1	6.7	23
SMCs								
Celestolide	1.7	2.9	95 \pm 14	103 \pm 8	97 \pm 9	5.0	7.4	14
Galaxolide	163	272	– ^c	100 \pm 16	112 \pm 6	4.0	15.6	18
Tonalide	11.5	21.2	– ^c	91 \pm 6	89 \pm 4	3.8	6.7	23
Musk xylene	3.7	8.6	– ^c	90 \pm 13	110 \pm 9	5.9	8.0	27
Musk moskene	1.0	2.3	98 \pm 12	107 \pm 4	100 \pm 5	2.7	4.0	19
Musk ketone	1.5	3.6	90 \pm 37	93 \pm 9	109 \pm 4	5.4	9.9	20
Bisphenols								
BPF	44.0	81.2	93 \pm 14	96 \pm 11	85 \pm 3	4.0	11.3	25
BPA	157	304	– ^c	89 \pm 8	89 \pm 9	10.0	11.7	25

^a Obtained for an air volume of 750 m³ (average air volume sampled).^b Low level corresponds with 5 $\mu\text{g L}^{-1}$; medium level corresponds with 50 $\mu\text{g L}^{-1}$, excepting for BPA 200 $\mu\text{g L}^{-1}$; and high level corresponds with 200 $\mu\text{g L}^{-1}$, excepting for BPA, which corresponds with 500 $\mu\text{g L}^{-1}$.^c Not calculated: amount in the composite sample was similar/ higher than spiking level or spiking level <LOD.^d Calculated at 50 $\mu\text{g g L}^{-1}$ for all the compounds, except for TiBP, DEP, TnBP, TCEP, Σ TCPP, DiBP, DBP, DMEP, BPA, TDCPP, BBP, TBOEP and DEHP (200 $\mu\text{g L}^{-1}$ level).

lower peak that could be attributed to an excessive vent. Then, a value of 30 mL min⁻¹ was selected as the most appropriate split flow because of being the one that provide a low baseline. Finally, T_{oven} values of 70 and 80 °C were tested, showing less tailed peaks when T_{oven} of 80 °C was used (Fig. S5c) and thus, it was selected for being the most suitable.

Furthermore, the GC oven temperature program used was based on the previously published by Sánchez-Piñero et al. [49] with some modifications due to the inclusion of new compound families (PAEs and SMCs) in the present study.

3.3. Optimization of SRM conditions

Optimum collision impact energies (in the second quadrupole) were optimized for each parent ions obtained after the first fragmentation (70 eV) for all the studied compounds, excepting for SMCs, that were based on a previous work (in preparation). After selecting the most abundant parent ions for each compound, product ion spectra (30 V for PAHs and 10 V for the remaining target compounds) were acquired to explore the fragmentation of each precursor ion, choosing those product ions that shown the highest abundance. To comply with the criteria set in

Commission Decision 2002/657/EC [85], four parent to product transitions were the objects subjected to optimization for each compound whenever possible. Collision energies were applied (in intervals of 5 V) from 5 to 30 V for bisphenols, OPFRs and PAEs; while they ranged from 5 to 80 V for PAHs because of being more resistant to fragmentation (Fig. S6-9). Collision energies that produced the most intense product ions for each precursor ion were chosen.

In Table 2 are shown the selected transitions quantification (Q) and confirmation (C) transitions used for each target compound, while in Table S1 are shown the ones selected for surrogate and internal standard compounds. Selection was made basing on the transition that provided the highest intensity, selectivity and better validation results. Moreover, ratio intensities between Q and C transitions were used as identification criterion to avoid overestimations or false positive findings in quantitative analysis according to the Decision 2002/657/EC [85]. In addition, Table S2 shows other optimized transitions that could be also used for quantification and confirmation.

3.4. Figures of merits

As is shown in Table 2, internal calibration graphs with respect to the corresponding surrogate using at least 7 calibration points were performed to evaluate linearity within the indicated linear range, achieving correlation coefficients $R^2 > 0.9942$ for all the studied compounds. Moreover, relative response factors (RRFs) with respect to the surrogates (calculated as the average of all the calibration range) were used to quantitate target compounds, showing satisfactory relative standard deviations (RSDs) <13.46 % (musk moskene) (Table 2). Nevertheless, RRFs were not calculated for DiBP, DBP and DEHP as the RRF model is not considered representative over the calibration range (RSD >20 %) [86], that might be attributed to blank levels found in filters. Therefore, solvent-based internal calibration was used for quantitating them. Matrix effect coefficients (MEC) were also estimated according to Kmellár et al. [87] by using internal calibration graphs slopes of matrix-matched and solvent standards. Matrix-matched standards were made by extracting blank filters (as commented in Section 2.4) and adding all target compounds, surrogates and internal standards over the dried residue (and sonicated for 3 min), while solvent standards were made directly using ethyl acetate. Attending to the values obtained (Table 2), negligible matrix effects (from -20 % to 20 %) were obtained for 15 of the studied compounds, while 22 compounds shown medium signal suppression (from -50 % to -20 %) and medium signal enhancement (from 20 % to 50 %) due to the matrix. Furthermore, strong signal suppression (below -50 %) for musk moskene, DMPEP, NPiPP, TDCPP, TBOEP, BaA and DOP, and strong signal enhancement (above 50 %) for Naph were obtained. Therefore, matrix-matched calibration was used for all the studied compounds except for DiBP, DBP and DEHP. Due to their high presence on blank filters, solvent-based calibrations were used for them. In addition, MEC could not be calculated for TEEDP due to calibration points above $150 \mu\text{g L}^{-1}$ were the only ones within the linear range when solvent-based standards were used. However, a strong signal enhancement was observed for TEEDP due to the matrix effect (Fig. S10).

The limits of detection (LODs) (mean blank + 3 SD criterion) and limits of quantification (LOQs) (mean blank + 10 SD criterion) for the proposed procedure were estimated by analysing 7 procedure blanks. The LOD and LOQ values ranged between $0.69 \text{ (BeP) pg m}^{-3}$ – $1130 \text{ (DBP) pg m}^{-3}$ and $1.2 \text{ (BeP) pg m}^{-3}$ – $1790 \text{ (DBP) pg m}^{-3}$, respectively (Table 3).

Trueness and precision were assessed by analysing a composite sample at three spiking levels: low ($5 \mu\text{g L}^{-1}$), medium ($50 \mu\text{g L}^{-1}$) for all compounds, excepting for BPA $200 \mu\text{g L}^{-1}$) and high ($200 \mu\text{g L}^{-1}$) for all compounds except for BPA $500 \mu\text{g L}^{-1}$). The composite sample were made by combining one circular piece (1.6 cm^2 diameter) of six different PM_{2.5} sampled filters collected on the sample place (Section 2.2). Selected filters covered all the sampling period, with an average PM_{2.5}

Table 4

Measured and certified values for SRM 1648a (n=4), experimental t-Student (t_{exp}), analytical recovery (R) and other compounds founded. In bold are $t_{\text{exp}} > 3.18$, which corresponds to t_{tab} (95% of confidence, two-tailed, n=4).

Compound	Found value \pm SD ($\mu\text{g g}^{-1}$)	Certified value \pm U_{exp} ($\mu\text{g g}^{-1}$)	$ t_{\text{exp}} ^a$	R (%)
Acy	0.098 \pm 0.015	0.173 \pm 0.012 ^b	9.98	56
Ace	0.13 \pm 0.010	0.25 \pm 0.083 ^{b,c}	24.08	51
Fl	0.140 \pm 0.032	0.251 \pm 0.035 ^b	6.89	56
Phe	3.94 \pm 0.15	4.86 \pm 0.17	11.7	81
Ant	0.521 \pm 0.073	0.459 \pm 0.013 ^b	1.71	114
Ft	7.23 \pm 1.24	8.07 \pm 0.14	1.36	90
Pyr	5.03 \pm 0.75	5.88 \pm 0.07	2.28	86
Ret	0.596 \pm 0.094	0.685 \pm 0.052 ^b	1.90	87
BaA	2.64 \pm 0.43	2.71 \pm 0.15	0.31	98
Chry	5.81 \pm 0.96	6.12 \pm 0.06	0.65	95
BbF + BjF	12.89 \pm 0.90	12.09 \pm 0.18 ^{b,c}	1.76	107
BkF	3.17 \pm 0.22	3.03 \pm 0.24	1.27	105
BeP	4.68 \pm 0.52	4.85 \pm 0.07	0.64	97
BaP	2.46 \pm 0.36	2.57 \pm 0.10	0.61	96
DBahA	0.50 \pm 0.01	0.47 \pm 0.49 ^b	2.14	113
IP	3.61 \pm 0.47	4.17 \pm 0.17	2.69	87
BghiP	4.25 \pm 0.71	5.00 \pm 0.18	2.12	85
TCEP	0.49 \pm 0.05 ^d			
TDCPP	0.22 \pm 0.02 ^d			
Galaxolide	0.22 \pm 0.04 ^d			
DBP	2.9 \pm 0.52 ^d			
BPF	0.20 \pm 0.03 ^e			
BPA	0.30 \pm 0.07 ^e			
DnHP	0.07 \pm 0.01			
TDCPP	0.18 \pm 0.01 ^e			
BBP	10.0 \pm 1.8			
DEHP	10.3 \pm 0.41 ^d			
TCrP	0.27 \pm 0.03			
DOP	0.88 \pm 0.05			

^a t_{exp} calculated as follows: $t_{\text{exp}} = \left| \frac{[\]_{\text{certified}} - [\]_{\text{found}}}{\text{SD}} \right| \times \frac{\sqrt{n}}$, where $[\]_{\text{found}}$ and SD are the mean and standard deviation of measured SRM 1648a values (n = 4) after applying the proposed method and $[\]_{\text{certified}}$ is the certified concentration.

^b Reference value.

^c The summation of [BbF + BjF] was calculated by using $[\text{BbF}]_{\text{certified}}$ and $[\text{BjF}]_{\text{certified}}$, reported individually in the SRM certificate. U_{exp} were also calculated as follows: $U_{\text{exp}[\text{BbF}+\text{BjF}]} = [\text{BbF} + \text{BjF}] \times \left(\frac{U_{\text{exp}[\text{BbF}]}}{[\text{BbF}]_{\text{certified}}} + \frac{U_{\text{exp}[\text{BjF}]}}{[\text{BjF}]_{\text{certified}}} \right)$, where

$U_{\text{exp}[\text{BbF}]}$ and $U_{\text{exp}[\text{BjF}]}$ are the reported U_{exp} for BbF and BjF, respectively.

^d Concentration < LOD (derived from field blanks).

^e Concentration LOD < x < LOQ (derived from field blanks).

mass concentration of $13.5 \mu\text{g m}^{-3}$. Attending to Table 3, successfully analytical recoveries were obtained for most of the studied compounds, within 83 % (Fl) – 115 % (DMPEP) and 85 % (TEHP) – 122 % (NPiPP) for medium and high spiking levels, respectively. Nevertheless, less satisfactory recoveries were accounted for DEP (64 %), BBP (50 %), TCEP (64 %), TEEDP (37 %), TBOEP (127 %) and TPPO (70 %) even considering the high spiking level. Similar recoveries were reported for TCEP and TPPO by Quintana et al. [47], that was suggested to be associated with a higher polarity. Naph were not included in the validation because of showing very low recoveries due to its high volatility. Moreover, intra-day (samples analysed the same day) and inter-day (samples analysed with a difference of one week) precision shown RSD <20% for most compounds except for DBP, NPiPP and BBP (between 21.6 % – 34.7 %) (Table 3). The expanded uncertainty (U_{exp}) for each pollutant was also estimated under inter-day conditions (n=6) using the semi-empirical approach [88] based on EURACHEM/CITAC guideline [89], considering a coverage factor of 2 (95 % of confidence). Volume uncertainties relative to the use of volume flasks and eVol® syringe to prepare solutions and for surrogate and internal standard addition to the sample were estimated assuming a rectangular distribution. Moreover, solid standards weighting, filter area taking, and air volume sampling uncertainties were also accounted by considering a rectangular distribution. Attending to values shown in Table 3, U_{exp} below 36 % were

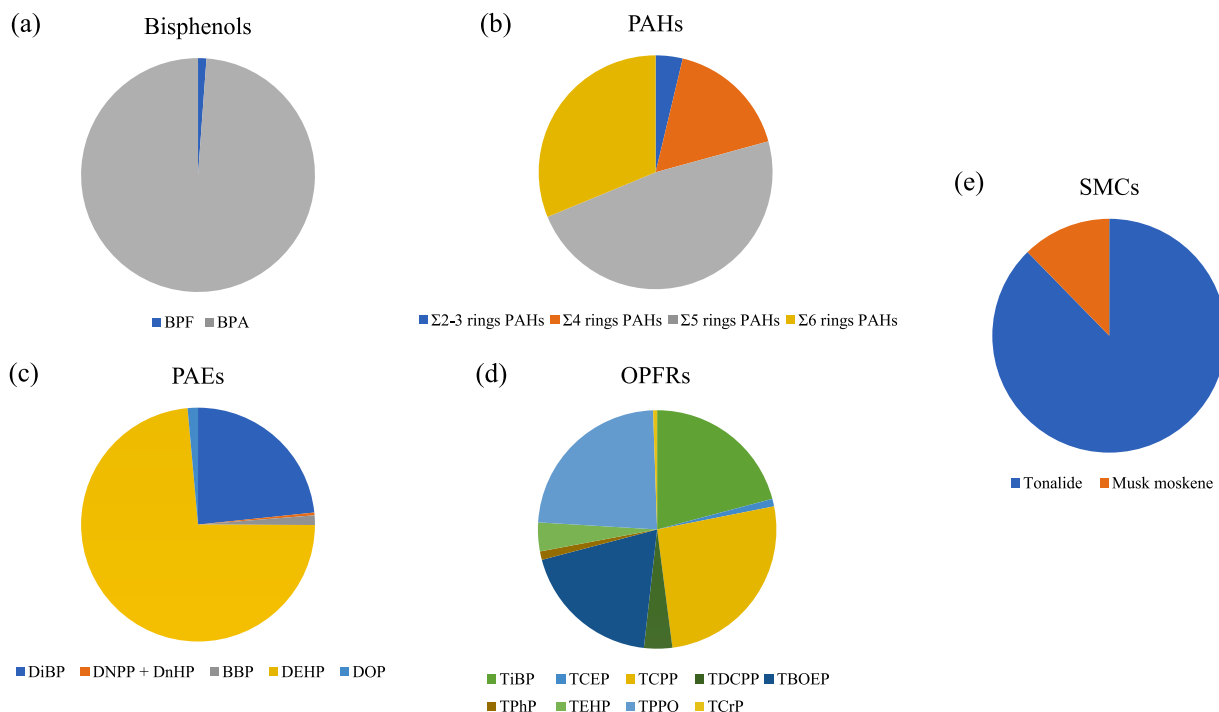


Fig. 2. Distribution of compounds within the different families found in analysed samples ($>LOQs$), concerning bisphenols (a), PAHs (b), PAEs (c), OPFRs (d) and SMCs (e). For PAHs, four main groups corresponding to rings number were considered: Σ_{2-3} rings PAHs (Acy, Phe, Ant and Ret), Σ_4 rings PAHs (Ft, Pyr, BaA and Chry), Σ_5 rings PAHs (Bbj, Bjf, BkF, BeP, BaP and DBahA) and Σ_6 rings PAHs (IP and BghiP)

obtained for most of the studied compounds. However, higher U_{exp} were obtained for DEP (75 %), BBP (104 %), TCEP (74 %), TEEDP (127 %), TBOEP (55 %) and TPPO (63 %) due to the analytical recoveries and inter-day precision observed for them.

3.5. Certified reference material analysis

Despite the lack of a PM reference material with certified values for the compounds included in the present study, accuracy of the proposed methodology for PAHs analysis was assessed by analysing the urban particulate matter standard reference material SRM 1648a four times within different days. In general, concentrations found after applied the proposed methodology are in good agreement with the certified and reference values after applying a t-Student test at 95 % confidence level and 3 degrees of freedom. Attending to Table 4, $|t_{exp}|$ values for PAHs from Ant to BghiP are lower than t_{tab} value of 3.18 (95 % confidence level, two-tailed and 3 degrees of freedom). Although value obtained for Phe was not statistically comparable with certified value, an acceptable analytical recovery of 81 % (with respect to the certified value) was obtained. Regarding the remaining PAHs, analytical recoveries with respect to the reported reference values were 56 %, 51 %, 56 % for Acy, Ace, Fl respectively. According to literature, extraction efficiency of these PAHs are noticeably influenced by temperature and pressure extraction conditions, that might cause variations in found concentrations of 332 %, 19 % and 66 % for Acy, Ace and Fl, respectively [90,91]. Then, recoveries of that PAHs might be attributed a result of not controlling these extraction variables in our methodology as well as because of their volatility [92].

Additionally, despite being only PAHs certified among all the compounds considered in the present study, other target compounds were found in SRM 1648a (Table 4), concerning 5 PAEs, 4 OPFRs, 2 bisphenols and 1 SMC. Within them, DEHP, BBP and DBP presented the highest concentrations (10.3, 10.0 and $2.9 \mu\text{g g}^{-1}$, respectively), while the lowest concentration was accounted for DOP ($0.27 \mu\text{g g}^{-1}$). To the best of our knowledge, information regarding these compounds were not found in the literature for SRM 1648a, then no comparisons could be

made.

3.6. Application to $PM_{2.5}$ samples

Among the 50 pollutants studied in the present work, a total of 34 compounds were found above LOQs at least in one of the analysed samples, comprising 16 PAHs, 9 OPFRs, 6 PAEs, 2 SMCs and both studied bisphenols (BPA and BPF). Considering the summation of the mean values obtained for each compound, pollutants families concentrations followed the order Σ_2 bisphenols (5060 pg m^{-3}) $>$ Σ_{16} PAHs (3370 pg m^{-3}) $>$ Σ_6 PAEs (2700 pg m^{-3}) $>$ Σ_9 OPFRs (1320 pg m^{-3}) $>$ Σ_2 SMCs (17.5 pg m^{-3}). Concerning the distribution of each pollutant within their family compound (Fig. 2), Fig. 2a shows that BPA was by far the most predominant when comparing with BPF, accounting for the 99 % of the Σ_2 bisphenols concentration. BPA concentrations found in the present study are higher than those reported from indoor $PM_{2.5}$ spaces ($600 - 1000 \text{ pg m}^{-3}$) [93] and atmospheric $PM_{2.5}$ collected from different metropolitan regions ($3.82 - 1650 \text{ pg m}^{-3}$) [94]. High bisphenols levels might be attributed to the industrial activity (involving activities such as spray painting and use of epoxy resins and plastics) in the area as being considered an important focus of exposure, especially to BPA [40,95]. Moreover, BPA concentrations obtained in the present study were in agreement to concentrations reported in air sampling filters collected from plastic factories (mean values between $4.7 - 7.9 \mu\text{g m}^{-3}$) [96]. Regarding PAHs, 5-6 ring number PAHs (Σ_{5-6} rings PAHs) represented the majority (79 %) of analysed PAHs, while 2-3 ring number PAHs (Σ_{2-3} rings PAHs) were found in less concentrations that might be attributed to their higher volatility (Fig. 2b), as reported in other studies [36,97]. Currently, there are no regulations concerning BaP or other pollutants in $PM_{2.5}$ samples. However, an annual limit for BaP in PM_{10} is set in 1.0 ng m^{-3} by European Directive 2004/107/EC [98], that was exceeded by just 1 analysed sample. Among PAEs, DEHP (1990 pg m^{-3}) was the most predominant, followed by DiBP (632 pg m^{-3}), while the remaining represented only the 3% of Σ_6 PAEs obtained (Fig. 2c). These findings are in agreement with those published by other authors in outdoor $PM_{2.5}$ samples [55,79,94]. Moreover, as it can be

seen in Fig. 2d, TCPP (345 pg m^{-3}), TPPO (311 pg m^{-3}), TiBP (276 pg m^{-3}), and TBOEP (253 pg m^{-3}) accounted for the 90 % of Σ_9 OPFRs quantitated. Some studies have already shown the occurrence of TCPP and TiBP in outdoor $\text{PM}_{2.5}$ from other areas, being two of the most profuse [79,99]. Moreover, only 2 SMCs were quantitated comprising tonalide and musk moskene (Fig. 2e), accounting for 15.4 and 2.2 pg m^{-3} by average, respectively. Although scarce studies were found regarding SMCs in atmospheric particles, the occurrence of tonalide has also been reported before in ambient air with an average concentration of 44 pg m^{-3} [100]. In addition, Ace, Fl, DMP, DEP, DBP, DMEP, DiPP, NPiPP, TPrP, TnBP, TEEp, celestolide, galaxolide, musk xylene and musk ketone were found below LOQs for all the studied samples.

4. Conclusions

The present study describes a novel and simple multi-residue procedure for the analysis of 50 organic compounds belonging to five different pollutants families in $\text{PM}_{2.5}$, providing successful validation results for most of the studied compounds. Moreover, due to the absence of a PM reference material that includes all the studied compounds, SRM 1648a was analysed for assess the accuracy of PAHs, obtaining a good agreement with the certified and reference values after applying a t-Student test for all PAHs except for Acy, Ace, Fl and Phe. Furthermore, some extraction parameters concerning d-SPE clean-up adsorbents and filters were studied (selecting Florisil® and nylon syringe filters, respectively), as well as PTV-GC-MS/MS conditions. Validation and applicability of the method were performed by using $\text{PM}_{2.5}$ samples of Vigo city. In general, target compounds concentrations found in samples were in agreement to data reported by other authors. Finally, this multi-pollutant approach could be and useful tool for monitoring a wide range of $\text{PM}_{2.5}$ -associated compounds, providing relevant information that could facilitate the comprehension between $\text{PM}_{2.5}$ composition and its harmful effect in human health.

Declaration of Competing Interest

The authors declare that this research has not conflicts of interests with any member of scientific community.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.talo.2021.100057](https://doi.org/10.1016/j.talo.2021.100057).

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