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Thermal desorption as an environmentally sound alternative for the determination of high production volume chemicals and polycyclic aromatic hydrocarbons in particulate matter

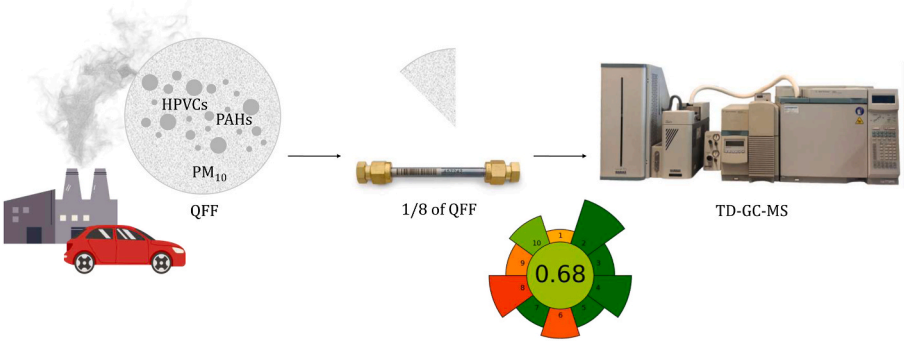
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HIGHLIGHTS

- Active sampling of HPVCs and PAHs in PM10 followed by TD-GC-MS was successfully applied.
- The TD-GC-MS method was positively evaluated using AGREEprep.
- Most of the target compounds were quantified in the Port of Tarragona.
- Phthalate esters (PAEs) were the compounds found at the highest concentrations.
- Benzenesulfonamides (BSAs) were detected in none of the air samples analysed.

GRAPHICAL ABSTRACT



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ABSTRACT

Particulate matter (PM) is a key component of air pollution, not only because of its own effects on human health but also because of certain semi-volatile organic compounds (SVOCs) which can be carried on its surface, such as benzothiazoles, phthalate esters (PAEs), ultraviolet stabilizers and polycyclic aromatic hydrocarbons (PAHs). Developing analytical methods for the determination of these compounds on PM samples is essential, especially in the light of current trends in the analytical processes such as automation and green chemistry. In this study, a method based on thermal desorption coupled to gas chromatography-mass spectrometry (TD-GC-MS) was developed and validated for the determination of 17 high production volume chemicals (HPVCs) and 13 PAHs at pg m^{-3} levels and evaluated using AGREEprep, with an overall score of 0.68.

The method was applied to PM_{10} air samples collected from the Port of Tarragona. The most representative target compounds were PAEs, accounting for 72% of the total and with the widest concentration ranges. Out of them, diethylhexyl phthalate (DEHP) was the most prevalent compound, with concentrations between 2647 pg

Abbreviations: benzothiazoles, BTHs; benzosulfonamides, BSAs; gas chromatography, GC; high production volume chemicals, HPVCs; liquid chromatography, LC; mass spectrometry, MS; microwave-assisted extraction, MAE; particulate matter, PM; phthalate esters, PAEs; polycyclic aromatic hydrocarbons, PAHs; polyurethane foams, PUFs; pressurised liquid extraction, PLE; quartz fibre filters, QFFs; selective ion monitoring, SIM; semi-volatile organic compounds, SVOCs; thermal desorption, TD; ultraviolet stabilisers, Tinuvins; volatile organic compounds, VOCs; ultrasonic-assisted extraction, USAE.

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m^{-3} and 5298 pg m^{-3}. The family of PAHs accounted for 17% of the total with a mean value of 9823 pg m^{-3}. Benzo(*a*)pyrene (BaP), which is regulated to a maximum annual average concentration of 1000 pg m^{-3} in PM_{10} by the European Directive , 2024/2881, was not detected in any of the samples analysed; hence, its concentration was below the regulatory limit.

1. Introduction

Sample preparation is a key step in analytical chemistry which consists in readying the sample for analysis with a specific equipment. This is especially important in situations where the analytes are found in trace concentrations in the original matrix, in which case a preconcentration will be needed, or in cases where the matrix itself can interfere with the analysis, and therefore the sample must be purified.

These preparation steps can be arduous and involve different manual processes which can introduce human error to the methods, so sample preparation is evolving towards the use of automated techniques with fewer steps and less chance of uncertainty. At the same time, the growing concern for environmental conservation is leading to the development of greener techniques which avoid the use of hazardous reagents, solvents and single-use materials, and try to reduce waste generation and energy consumption (López-Lorente et al., 2022).

In the case of air samples and their preparation, it is common to use techniques with an on-site preconcentration step onto a solid, the nature of which will depend on the analytes (Galvão et al., 2018). Certain analytes can be found in equilibrium between both the gas and particle phases of air, due to their semi-volatile nature (Goss, 2004; García-Garcinuño et al., 2024a; dos Santos Souza et al., 2021). That is the case of semi-volatile organic compounds (SVOCs), which can exist either in their gaseous form or adhered to the surface of particulate matter (PM), and enter deeply into the respiratory system through it (Ramírez et al., 2011). These compounds are preconcentrated using high-volume air samplers, to retain the PM on quartz fibre filters (QFFs) and the gas phase on polyurethane foams (PUFs) (García-Garcinuño et al., 2024a; Ramírez et al., 2011; Maceira et al., 2018; Mantis et al., 2005; Naccarato et al., 2021), or by passively allowing their retention on PUFs through molecular diffusion (García-Garcinuño et al., 2024b).

Some of these SVOCs are high production volume chemicals (HPVCs) (García-Garcinuño et al., 2024a; Maceira et al., 2020a), products employed in large quantities in the plastics industry with a wide range of chemical properties, including families such as benzothiazoles (BTHs) (Maceira et al., 2018; Li et al., 2020), phthalate esters (PAEs) (Zhang et al., 2014), benzosulfonamides (BSAs) (García-Garcinuño et al., 2024a; Maceira et al., 2018), and ultraviolet stabilisers (Tinuvins) (Li et al., 2020). They have been linked to health effects such as damage to the respiratory system (Liao et al., 2018), hormone imbalance (Liu et al., 2014) or carcinogenicity (Hou et al., 2021; Núñez et al., 2022).

Other SVOCs found in PM samples are polycyclic aromatic hydrocarbons (PAHs), released by incomplete combustion of fossil fuels and studied due to their carcinogenicity (Moradi et al., 2022). In fact, one of them, benzo(*a*)pyrene, is the only semi-volatile organic pollutant with an average annual concentration in PM_{10} limited by law in the European Union (EU) (Directive (EU), 2024), with a maximum of 1000 pg m^{-3} due to its classification as a probable human carcinogen (Agents Classified by the IARC, 2022).

These SVOCs are typically desorbed from the QFFs using organic solvent desorption techniques such as pressurised liquid extraction (PLE) (García-Garcinuño et al., 2024a; Ramírez et al., 2011; Maceira et al., 2018; Aragón et al., 2012), Soxhlet (Anh et al., 2020; Wong et al., 2018), microwave-assisted extraction (MAE) (Naccarato et al., 2021) or ultrasonic-assisted extraction (USAE) (Mantis et al., 2005), followed by determination by gas chromatography coupled to mass spectrometry (GC-MS) (Núñez et al., 2022; García-Garcinuño et al., 2025) or liquid chromatography coupled to mass spectrometry (LC-MS) (Herrero et al., 2014). These extraction techniques require the use of organic solvents, which can be harmful to the environment and hazardous to the operator, and usually involve filtration, evaporation and/or reconcentration steps which, as mentioned above, are performed manually and can add human error.

Thermal desorption (TD) is a technique more commonly used for desorption of volatile organic compounds (VOCs) from adsorbents such as graphitised carbon (Vallecillos et al., 2019), but has also been used for desorption of SVOCs from phenyl phenylene oxide (known as TENAX®) (Jia et al., 2023; Aragón et al., 2013). This study proposes this technique as an automated and more environmentally friendly alternative to extraction of QFFs using organic solvents. Its main advantages are this greenness and automation, the shorter manipulation time, and the fact that the whole amount of sample placed inside the desorption tube is injected into the GC-MS, so, ideally, lower instrumental limits of detection (LODs) and quantification (LOQs) are expected. There are two main commercially available types of thermal desorbers, those where the sample is directly desorbed into the injection port, and those where there is a transfer line between the TD and the GC-MS instrumentation. Some SVOCs can experience carryover, the condensation or adsorption of the analytes in the flow path, in instrumentation of the second kind (Application Note 006, 2014; Application Note 108, 2014), but previous studies with this type of instrumentation have shown good linearity for certain families of compounds, such as PAHs (Flores and Mertoglu, 2020) or PAEs (Aragón et al., 2013).

This study aims to adapt the established sampling and analysis methods used in previous literature (García-Garcinuño et al., 2024a, 2025), applying this hands-off sample preparation to a wide range of SVOC families. Therefore, the main goals of this study are (1) to study the viability of thermal desorption as an alternative technique for the determination of HPVCs and PAHs adhered to PM_{10} (particle size $\leq$ to 10 mm) retained in quartz fibre filters, (2) to develop and validate a multi-residue method for this determination by TD-GC-MS, (3) to evaluate the greenness of the developed method, and (4) to apply it to the analysis of samples from the Port of Tarragona.

2. Experimental part

2.1. Reagents and standards

The studied HPVCs are five benzothiazoles (BTHs): benzothiazole (BTH), 2-chlorobenzothiazole (ClBT), 2-(methylthio)benzothiazole (MeSBT), 2-aminobenzothiazole (NH_2BT), and 2-hydroxybenzothiazole (OHBT); three benzenesulfonamides (BSAs): benzenesulfonamide (BSA), *N*-methyl-*para*-toluenesulfonamide (Me-*p*-TSA), and *para*-toluenesulfonamide (*p*-TSA); six phthalate esters (PAEs): dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DiBP), diethylhexyl phthalate (DEHP), and di-*n*-octyl phthalate (DnOP), plus diethylhexyl adipate (DEHA); and six ultraviolet stabilisers (Tinuvins): 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole (UVP), 2-(2H-benzotriazol-2-yl)-4-methyl-6-(2-propenyl)phenol (Allyl-BZT), 2-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-2H-benzotriazole (UV320), 2-*tert*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UV326), 2-(2H-benzotriazol-2-yl)-4,6-di-*tert*-pentylphenol (UV328), and 2,4-di-*tert*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol (UV327). Eighteen polycyclic aromatic hydrocarbons (PAHs) were studied: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz(*a*)anthracene (BaA), chrysene (Chr), benzo(*b*)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(*j*)fluoranthene (BjF), benzo(e)pyrene

(BeP), benzo(*a*)pyrene (BaP), dibenz[a,h]anthracene (DiB), indeno [1,2,3-cd]pyrene (InD), and benzo[ghi]perylene (BghiP). The compounds were mostly purchased from Sigma Aldrich (Steinheim, Germany), except for UV320 and BHT-CHO, which were obtained from LGC Standards (Barcelona, Spain) at purities always over 96%

Individual stock solutions of all compounds of approximately 2000 mg L^{-1} were prepared in ethyl acetate, except for the ones of PAHs which were prepared in hexane. Working solutions of 100 mg L^{-1} in ethyl acetate were prepared for each family of compounds. All solutions were stored at −19 °C until use.

GC-grade ethyl acetate and hexane were obtained from Carlo Erba Reagents (Cornaredo, Milan, Italy) with purity >99.9%. Helium and nitrogen gases used for the chromatographic analysis and the cryogenisation of the trap were purchased with 99.999% purity from Linde (Barcelona, Spain).

2.2. Sampling

The Port of Tarragona lies at a key point on the Northern Mediterranean coast of the Iberian Peninsula, with direct rail, air and sea connections to strategic locations in the North-western European territory (Port Tarragona, 2025). Its closeness to Tarragona's North and South industrial parks, the biggest chemical complex in Southern Europe (AEQT, 2025), means that large amounts of the produced and consumed products are shipped through the Port. In fact, during 2024, 31.67 million tonnes of cargo were handled by the Port, out of which 9.23 million tonnes were solid bulk, including coal, and 7.03 million tonnes were cereals, flours, feed and fodder (Port Tarragona, 2025), the main traffic items from which PM can originate.

Air PM_{10}-fraction samples were collected from the sampling point in the Port of Tarragona over a period of two months (November-December 2024), with a total of ten 24-h samples. The equipment used for collection of the samples was an MCV-PM10 High-Volume Air Sampler (MCV S.A., Collbató, Spain). The filters used for deposition of PM_{10} were 150-mm-diameter QFFs purchased from Whatman (Sigma Aldrich). Once QFFs were sampled, they were stored in aluminium foil and properly labelled to be kept in the freezer at −19 °C until analysis.

2.3. Thermal desorption and chromatographic analysis

One-eight portions of the sampled QFFs were cut into small pieces using sterilised scissors and introduced into empty stainless-steel tubes of 9 cm of length, 6.35 mm of outer diameter and 4.5 mm of inner diameter (Markes International, Cardiff, UK) using sterilised tweezers. The tubes were desorbed using an Ultra Xr TD autosampler coupled to a Unity 2 TD, both from Markes International. The desorption method included a pre-purge of 1 min with a helium flow of 20 mL min^{-1} with a split of 5 mL min^{-1}, followed by the 10 min tube desorption to 330 °C in splitless mode to a mixed TENAX® and graphitised carbon trap (Markes International) at −25 °C. Then, the trap was desorbed in 10 min at 330 °C with a 5 mL min^{-1} split. The helium flow automatically carried the target analytes through the flow path at 180 °C into the 6890 N GC system (Agilent technologies, Santa Clara, CA, USA). The chromatographic separation was performed with a ZB-50 (50% phenyl-50% dimethylpolysiloxane) capillary column (30 m × 0.25 mm; 0.25 μm) from Phenomenex (Torrance, CA, USA) under a constant flow-rate of 1.2 mL min^{-1}. The temperature of the oven started at 80 °C and was increased at a rate of 5 °C min^{-1} to 275 °C, and then at a rate of 20 °C min^{-1} to 310 °C, at which it was maintained for 10 min. The total duration of the chromatographic separation was 50.75 min. The detection was performed using a 5973 inert mass spectrometer with triple-axis detector from Agilent technologies (Santa Clara, CA, USA) in SIM mode with a filament-multiplier delay of 8 min. The transfer line temperature was fixed at 280 °C, the electron ionisation source used an energy of 70 eV at 230 °C and the analyser temperature was 150 °C.

2.4. Quality assurance/quality control (QC/QA)

To avoid cross-contamination, the QFFs were conditioned before sampling by placing them in a muffle at 450 °C overnight, covered in aluminium foil, and stored at −19 °C until use. All glassware material used for calibration was previously washed by ultrasonication with isopropanol. For quality assurance purposes, instrumental and procedural blanks were performed periodically. The target analytes were not detected in any of the blanks, demonstrating a lack of background contamination. Standard controls of 100 ng were also included in the GC-MS batches to verify proper instrument performance.

For quantification of the analytes, standards of different concentration levels were prepared from the stock solution to build the external standard calibration curves. Specifically, standard solutions in the 0.05 to 1000 mg L^{-1} range were prepared to set the limits of detection (LOD) and quantification (LOQ) and the linear range. Each QFF was cut into 1/8 portions using sterilised scissors, and each portion was spiked with 1 μL of the corresponding standard solution to have between 0.05 and 1000 ng per portion. The spiked QFFs were left to dry and, once the solvent had evaporated, they were cut into small pieces and introduced into the empty stainless-steel tubes using sterilised tweezers.

3. Results and discussion

3.1. Method optimisation

3.1.1. Gas chromatography

To optimise the chromatographic separation, a mixed solution of 10 mg L^{-1} of the target HPVCs was prepared in ethyl acetate, and 1 μL was injected directly in the GC-MS system. Several oven temperature programs were tested based on the prior experience of our research group with the determination of these compounds (García-Garcinuño et al., 2024a). All compounds were successfully separated within 50.75 min using the chromatographic separation described in Section 2.3. Initially, MS in full scan mode was first performed to compare the mass spectra obtained by electron ionisation fragmentation with those available in the NIST MS library. Subsequently, selective ion monitoring (SIM) mode was selected for increased sensitivity. Each target compound was identified by its retention time, the most abundant ion *m/z* used for quantification, and two or three qualifier ions with their relative abundances to the corresponding quantifier ion. These optimised identification parameters, obtained from direct injection, are summarised in Table 1S.

3.1.2. Thermal desorption

TD optimisation was performed by spiking 1/8 portions of a QFF with the different families of target compounds at a 10 ng. The initially applied TD conditions were based on the ones reported by Aragón et al. (2013) for the determination of SVOCs in the gaseous phase of air using TENAX® adsorbent tubes and a focusing trap of the same material. They did a tube desorption at 320 °C for 10 min with a helium flow of 50 mL min^{-1} in splitless mode, into the TENAX® trap at 0 °C. The trap was then desorbed for 5 min at 320 °C, with a split of 5 mL min^{-1}. Due to the use of a different adsorbent, the TENAX® trap was replaced by a mixed TENAX®/graphitised carbon trap, and the TD parameters had to be optimised. Tube and trap desorption temperatures were fixed at 330 °C to ensure desorption of the target analytes, and the trap desorption mode was fixed to the smallest possible split (5 mL min^{-1}) as recommended by the supplier, to avoid column contamination and to prolong its lifetime. The trapping temperature was decreased to −25 °C to ensure retention of the analytes in the focusing trap. The TD parameters optimised were the following: tube desorption time and flow-rate, and trap desorption time.

Initially, the tube desorption was carried out at 5, 10 and 15 min, while the other TD parameters were fixed as the initial ones. The results showed a notable increase in the peak areas of the heavier target compounds, *e.g.* UVP, BeP and BeaP, when the desorption time was increased

from 5 to 10 min, with the stabilisation of the response at 15 min. In order not to lengthen the tube desorption step, 10 min was chosen as the optimal time. Then, three tube desorption helium flow-rates, 20, 50, and 100 mL min^{-1}, were tested in splitless mode. The highest peak areas were observed at flow-rates of 20 mL min^{-1} and 50 mL min^{-1} depending on the target compound. In contrast, a decrease in peak areas was detected for all compounds at a flow-rate of 100 mL min^{-1}. The peak areas that are maximised at 50 mL min^{-1} are those of the heavier compounds, *e.g.* DEHP, UV327 and BaP, as they need a higher flow rate to favour their desorption from the QFF. However, to avoid compromising the signal of the lighter compounds, a flow-rate of 20 mL min^{-1} was selected as optimal. Finally, three trap desorption times, 5, 10 and 15 min, were tested. The highest peak areas were obtained at 10 and 15 min, with comparable values between them. Therefore, 10 min was fixed as the optimal to reduce the overall method duration.

Carry-over tests were performed under the optimised desorption conditions by performing a second desorption of the TD tube, which was filled with 1/8 portion of QFF previously spiked with the highest calibration level (1000 ng). Regardless of the target compound, the peak areas found in the second desorption were lower than 5%, confirming complete desorption of the compounds under the optimised tube desorption conditions. However, even under optimised conditions, target compounds such as the BTHs NH_2BT and OHBT, as well as the PAHs Nap, Acy, DiB, InD and BghiP, were lost during the desorption step. The most volatile ones, *e.g.* Nap and Acy, could be lost in the tube desorption step, since the traps most used for volatile compounds are made up only of graphitised carbon, a sorbent with stronger retention capacity (Vallecillos et al., 2019). Higher molecular weight compounds, such as InD and BghiP, could have been retained in the long transfer line between the TD and GC instruments (trap desorption step), a key feature of Markes instruments. These compounds might slowly desorb from the transfer line over time, slightly increasing the baseline of the chromatogram without interfering with the identification and quantification of the target compounds. TD was considered unsuitable for these compounds and the method was further developed only for those that could be reliably detected with sufficient sensitivity (see Table 1).

3.2. Validation

In order to validate the TD-GC-MS method, the instrumental limits of detection (LODs) and quantification (LOQs), the method detection limits (MDLs) and method quantification limits (MQLs), linear ranges and repeatability (relative standard deviation percentage, RSD%) were determined for the target compounds.

The linear ranges of the method as well as the LODs and LOQs were obtained by analysing 1/8 portions of QFF spiked at different concentration levels, following the procedure described in Section 2.4. Good linearity was achieved for all the target compounds, as shown in Table 2S, from their respective LOQs up to 500 or 1000 ng. In some cases (BT, ClBT and DEHA), two calibration curves were obtained for two different linear ranges. All calibration curves were obtained with coefficients of determination (r^2) higher or equal to 0.990. As Table 2S shows, the LOQs were between 0.1 ng and 50 ng. LODs were fixed as the lowest observed non-linear concentration with signal at least three times greater than the signal of noise, between 0.05 ng and 10 ng. Repeatability was evaluated by spiking five 1/8 portions of QFF at 1, 10 and 50 ng, depending on the target compound. Regardless of the concentration level, the developed method showed good precision for all target compounds, with % RSD values below or equal to 17 % in all cases. The obtained results comply with the requirements of RSD% values lower than 25% established by the USEPA (Compendium Method TO-17, 1999) performance guidelines for VOCs and SVOCs determinations.

MDLs and MQLs were estimated from instrumental LODs and LOQs and the sampling volume of 720 m^3 applied. MDLs, as Table 1 shows, were found to be between 0.56 pg m^{-3} and 111 pg m^{-3}, while MQLs ranged from 1.11 pg m^{-3} to 556 pg m^{-3}. The MDLs and MQLs from this study were compared to those reported by García-Garcinuño et al. (2024a) using PLE-GC-MS, which ranged from 0.2 pg m^{-3} to 77 pg m^{-3} and 0.6 pg m^{-3} and 154 pg m^{-3}, respectively. As Table 1 shows, some of the compounds such as DEHA, DEP, UV326 and lighter PAHs (from Ace to BaA), have significantly lower limits with TD-GC-MS. Others like ClBT, *p*-TSA, DMP and Pyr have similar limits regardless of the analytical method used. In contrast, higher molecular weight PAHs (from Chr to BaP) and most Tinuvins, for instance, showed better limits with PLE-GC-MS. Moreover, as observed with the PAHs, the limits obtained by TD-GC-MS progressively increased with molecular weight, likely due to partial retention of heavier compounds in the transfer line.

Table 1
Method detection limits (MDLs) and method quantification limits (MQLs) for each target analyte in pg m^{-3}. A comparison between TD-GC-MS and PLE-GC-MS (García-Garcinuño et al., 2024a).

Compound	MDL		MQL	
	TD-GC-MS	PLE-GC-MS	TD-GC-MS	PLE-GC-MS
BTH	2.8	0.6	11	1.6
ClBT	0.6	0.4	1.1	0.9
MeSBT	0.6	0.2	1.1	0.6
BSA	111	17	556	25
Me-*p*-TSA	111	5.6	556	11
***p*-TSA**	2.8	3.1	11	76
DMP	1.1	1.2	11	47
DEP	11	58	111	166
DiBP	11	0.4	111	0.9
DEHA	5.6	51	11	77
DEHP	111	0.7	556	68
UVP	111	25	278	62
Allyl-BZT	111	25	278	62
UV320	28	2.4	83	3.2
UV326	11	20	111	68
UV328	11	7.6	83	15
UV327	111	15	556	22
Ace	0.6	0.9	1.1	2.5
Flu	0.6	2.4	1.1	8.1
Phe	0.6	0.8	1.1	1.6
Ant	0.6	1.7	1.1	8.3
Fla	0.6	2	1.1	6.6
Pyr	1.1	1.4	11	2
BaA	11	3.2	111	16
Chr	11	7.6	111	76
BbF	28	6.6	111	20
BkF	111	24	278	80
BjF	111	7.7	278	15
BeP	11	7.9	556	16
BaP	111	77	556	154

3.3. Greenness evaluation

Given that one of the main goals of this study was to assess the greenness of TD as a sample preparation technique for determining the target compounds in PM_{10} air samples, both the method developed in the present study and the one of García-Garcinuño et al. (2024a) using PLE were evaluated. The metric tool proposed by Pena-Pereira et al. (2022) and Wojnowski et al. (2022), AGREEprep - Analytical GREEnness Metric for Sample Preparation, was used to fulfil this purpose. Ten features of both sample preparation methods, corresponding to the ten principles of Green Sample Preparation (López-Lorente et al., 2022), were rated on a scale from 0 to 1, with 1 representing the ultimate environmentally-sound performance. Each of these criteria was used to calculate the overall score with an assigned default weight, where 1 represents the best performance as well.

The overall score (Fig. 1) clearly showcases the greenness of using TD (0.68) against using PLE (0.16). Several factors contribute to these scores, with criterions 1, 5, 6, 8 and 9 being similar for both methods since they assess their common characteristics. On site sampling preparation with a preconcentration step has a score of 0.33. The low sample amount (<0.1 g) gives the highest score of 1.0 to both methods. But both

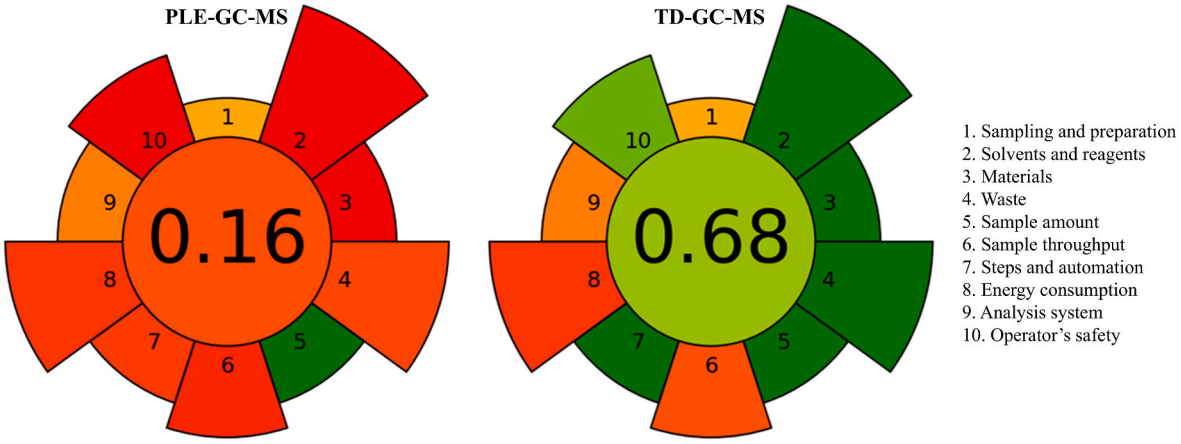


Fig. 1. Greenness evaluation diagrams. PLE-GC-MS *versus* TD-GC-MS.

methods have low sample throughputs, since the automated TD preparation lasts 30 min allowing two samples per hour (score of 0.16) and the full PLE preparation lasts 40 min allowing only 1.5 sample per hour (score of 0.1). In both methods, there is high energy consumption, since TD instrumentation is used in one case and PLE, rotary evaporator and fume hood are used in the other, giving a low score for this criterion. The post-sample preparation configuration for analysis is GC-MS in both cases, with a score of 0.25.

For all other criterions, the performance of TD is significantly better. No hazardous or single-use materials are employed in TD, giving a score of 1.0 to criterions 2 and 3. On the other hand, for PLE-GC-MS more than 10 mL of hazardous solvents and reagents (dichloromethane and dimethylformamide) are used, and even if the used materials are renewable, most of them can only be used once to avoid cross-contamination, so both these criterions have a score of 0.0. Criterion 4 is related to contaminated waste; in the case of TD this is null, so the score is 1.0, while in the case of PLE the contaminated waste includes the sampled filter and the consumable materials such as PTFE filters or micropipette tips, amounting to about 20 g and giving the method a score of 0.14 in this criterion. In TD, the preparation has less than 2 steps and is automated, giving criterion 7 a score of 1.0, while when using PLE there are 5 steps and semi-automation was selected because only the extraction is automated, giving a score of 0.12 to this criterion. Finally, for criterion 10, in TD there is only one operational hazard, the high temperature of the TD instrumentation (0.75), while in PLE there are multiple chemical hazards related to the organic solvents used, and electrical and thermal hazards related to the PLE and rotary evaporator instrumentation (0.0).

3.4. Application to PM_{10} air samples

The developed method was used to study the presence of the target HPVCs and PAHs in 10 p.m.$_{10}$ samples from the Port of Tarragona. Table 2 shows the arithmetic mean (pg m^{-3}), median (pg m^{-3}), concentration range (pg m^{-3}) and detection frequency (DF %) of the target compounds detected in at least one of the PM_{10} samples analysed.

The total concentrations of the target compounds were in the range of 8201 pg m^{-3} and 14,153 pg m^{-3} with a mean value of 9823 pg m^{-3}. As Table 2 shows, the most representative target compounds were PAEs with sum values (∑PAEs) ranging between 5736 pg m^{-3} and 10,902 pg m^{-3}. The arithmetic mean value of ∑PAEs was 7098 pg m^{-3}, accounting for 72% of the total. The family of PAHs (∑PAHs) accounted for 17% of the total with a mean value of 9823 pg m^{-3} and concentrations in the range of 1054 pg m^{-3} and 2213 pg m^{-3}. Tinuvins (∑Tinuvins) and BTHs (∑BTHs) accounted for 9% and 2% of the total with mean values of 867 pg m^{-3} and 174 pg m^{-3}, respectively. The concentration range of these two families of compounds was between 65 pg m^{-3} and 1092 pg m^{-3}. Certain Tunuvins and PAHs, such as UV326 and BjF, had high detection frequencies even if they were detected in non-quantifiable amounts.

Table 2
Arithmetic mean (AM), median (Med), concentration range (CR) and detection frequency (DF) of the target analytes in PM_{10} air samples from the Port of Tarragona.

Compound	Concentrations (pg m^{-3})			DF (%)
	AM	Med	CR	
BTH	167	122	65.1 - 356	100
ClBT	7.32	0.28	n.d. - 70.7	10
∑BTHs	174	123	65 - 356	-
DMP	105	93.8	77.6 - 153	100
DEP	573	604	239 - 789	100
DiBP	1150	1096	752 – 1833	100
DEHA	1861	1752	1567 – 3125	100
DEHP	3410	3250	2647 – 5298	100
∑PAEs	7098	6833	5736 – 10,902	-
UVP	444	399	355 - 580	100
Allyl-BZT	148	< MQL	n.d. - 373	30
UV320	89.7	88.0	< MQL - 125	100
UV326	< MQL	125	< MQL - 174	100
UV328	< MQL	< MQL	< MQL - 144	100
∑Tinuvins	867	838	588 – 1092	-
Phe	85.8	83.4	54.4 - 145	100
Ant	70.0	68.7	60.3 - 83.7	100
Fla	127	119	66.7 - 211	100
Pyr	202	201	120 - 331	100
BaA	184	179	143 - 211	100
Chr	329	320	227 - 466	100
BbF	273	260	189 - 344	100
BkF	282	312	< MQL - 355	100
BjF	< MQL	<MQL	n.d. – <MQL	90
∑PAHs	1683	1697	1054 – 2213	-
Total	9823	9559	8201 – 14,153	-

Fig. 2 shows the mean, 25th, 50th and 75th percentiles, as well as the maximum and minimum concentrations of each target compound. In general, the target compounds followed a positively skewed asymmetric distribution of the results, with arithmetic means higher or slightly higher than the median. Only three compounds, DEP, UV326 and BkF, showed a negatively skewed asymmetric distribution (arithmetic mean < median). Allyl-BZT, UV328 and BjF, followed a symmetric distribution (arithmetic mean = median). PAEs were the compounds found at the highest concentrations with individual arithmetic means between 105 pg m^{-3} and 3410 pg m^{-3}, and DFs of 100%. PAEs had the widest concentration ranges, with values between 77.6 pg m^{-3} and 5298 pg m^{-3} depending on the compound. The lower and upper whiskers of the PAEs concentration boxes in Fig. 2 indicate the presence of concentration peaks at both low and high levels in the PM_{10} samples analysed.

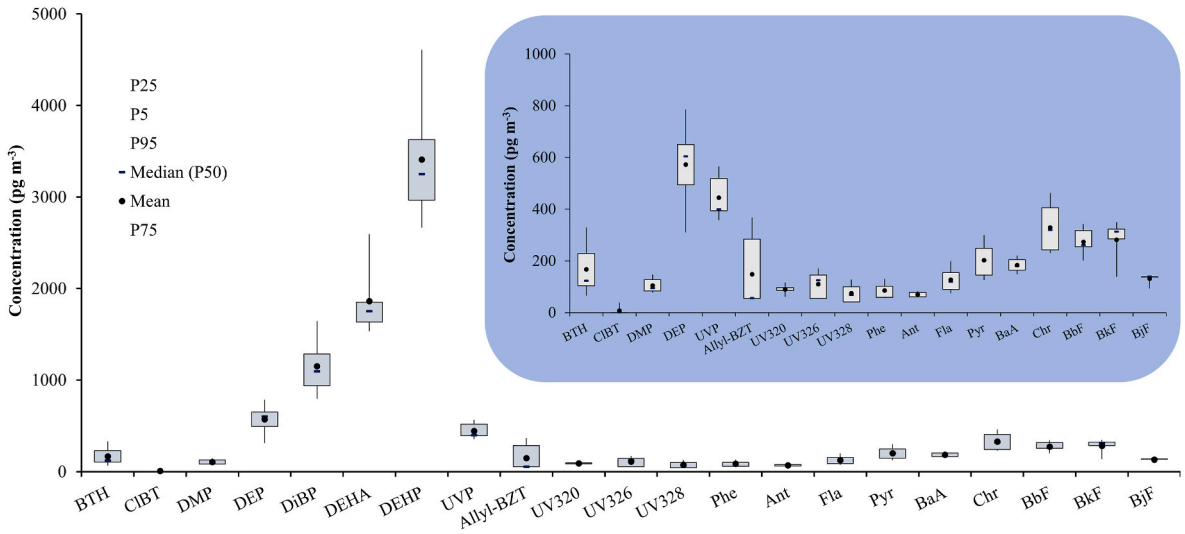


Fig. 2. Percentile distribution of the concentrations of the target compounds found in the PM_{10} samples analysed. Highlighted in blue, the distribution of concentrations of those compounds found in lower concentrations, without DiBP, DEHA and DEHP.

DEHP was the most prevalent compound, with concentrations between 2647 pg m^{-3} and 5298 pg m^{-3}. On the other hand, the BSAs included in the study, MeSBT, UV327, Ace, Flu, BeP and BaP were not detected in any of the sample analysed. Regarding BTHs, only BTH was found in all samples with an arithmetic mean of 167 pg m^{-3} and ClBT was found at 70.7 pg m^{-3} in a single sample.

Other compounds found in notable concentrations included certain Tinuvins and PAHs. UVP and UV320 were the most characteristic Tinuvins, with DFs of 100% and arithmetic mean concentrations of 444 pg m^{-3} and 89.7 pg m^{-3}, respectively. Allyl-BZT showed the widest concentration range among the Tinuvins (see Fig. 2), but its arithmetic mean was <MQL because it was the least detected (DF = 30%). All the PAHs detected in the PM_{10} samples analysed showed 100% DFs, except for BjF which had a DF of 90%. The arithmetic mean concentrations for PAHs were in the range of 70.0 pg m^{-3} and 329 pg m^{-3}. In general, the concentration boxes of PAHs were narrow (*e.g.* Ant and BaA) or intermediate (*e.g.* Pyr and Chr) with values between 54.4 pg m^{-3} and 466 pg m^{-3}. BjF was only found at not quantifiable levels (<MQL). It is important to note that BaP is regulated to a maximum annual average concentration of 1000 pg m^{-3} in PM_{10} by the European Directive , 2024/2881 on ambient air quality and cleaner air for Europe (Núñez et al., 2022). Since BaP was not detected in the samples analysed, its concentration was well below the regulatory limit.

Previous literature shows similar trends in the concentration of SVOCs found in 2-month passive air samples from El Serrallo, the urban area closest to the Port of Tarragona, where PAEs were the most abundant family followed by PAHs (García-Garcinuño et al., 2025). The authors also reported that DEHP and DEHA were the PAEs found at the highest concentrations, with annual mean concentrations of 7.40 ng m^{-3} and 6.80 ng m^{-3}, respectively. The detection of concentration peaks throughput the year resulted in a wide concentration range, 1.9 ng m^{-3} and 18.9 ng m^{-3}, and a higher mean concentration than in the present study. The concentrations of PAHs that they found were stable over time, with values between 0.16 ng m^{-3} and 2.30 ng m^{-3}, and BaP always remained below the 1 ng/m^{-3} set by the European Directive (EU), 2024/2881. Maceira et al. (2019) reported slightly lower Tinuvin concentrations (6.5-196 pg m^{-3}) than in the present study when analysing 24-h PM_{10} samples from the Port of Tarragona. Nevertheless, certain trends were consistent: UVP, UV320 and UV328 were detected in 90-100% of the samples analysed, with UVP being the most abundant. In contrast, allyl-BZT was detected in only 10% of the samples and always at non quantifiable levels. In a posterior study, Maceira et al. (2020b) found BTH and ClBT concentrations between non quantifiable levels and 3088 pg m^{-3} in 24-h PM_{10} samples from the same sampling site, with mean concentrations of 969 pg m^{-3} and 69 pg m^{-3}, respectively. These values were higher than those in the present study, but the variability in the presence of these compounds is consistent. A long-term monitoring would be necessary for a more robust comparison.

4. Conclusions

A multi-residue method based on TD-GC-MS was developed and validated for the determination of 17 HPVCs and 13 PAHs in PM_{10} air samples at pg m^{-3} concentrations.

Most of the originally targeted compounds were identified and quantified with good linearity, with r^2 higher or equal to 0.990. The validated method was compared to previous studies using PLE-GC-MS, and the MDLs and MQLs reached with TD-GC-MS were comparable or lower, with the exception of some of the heaviest compounds. Nevertheless, this was not a problem for the quantification in the PM_{10} samples analysed as the analytes were present at values above the limits of the analytical method developed.

The key feature of TD as a preparation technique is its greenness, as evaluated by AGREEprep in comparison to PLE-GC-MS, and its automation that allows for a faster and less arduous sample preparation, including fewer manual steps. Analytical chemistry is moving towards hands-off approaches and a decrease in the use of harmful reagents and single-use materials, a trend greatly showcased by this TD-GC-MS method.

Both the method validation and the evaluation of method greenness highlight the viability of TD-GC-MS as an environmentally friendly alternative for the analysis of certain families of SVOCs in PM_{10} air samples.

CRediT authorship contribution statement

Laura Solé-Domènech: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Conceptualization. **Laura Vallecillos:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Conceptualization. **Alexandre Fabregat:** Writing – review & editing, Supervision, Investigation. **Francesc Borrull:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2026.144865.

Data availability

Data will be made available on request.

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