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Simultaneous Determination of Polycyclic Aromatic Hydrocarbons, Alkylphenols, Phthalate Esters and Polychlorinated Biphenyls in Environmental Waters Based on Headspace – Solid Phase Microextraction Followed by Gas Chromatography – Tandem Mass Spectrometry

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Abstract

In the present work, a sensitive, simple, and fast method with little sample handling has been developed for the determination of 34 semi-volatile organic xenobiotics from rain, sea and ground waters. The method is based on Headspace-Solid Phase Microextraction (HS-SPME) and Gas Chromatography coupled to Mass Spectrometry (GC-MS/MS). Sixteen Polycyclic Aromatic Hydrocarbons (PAHs), eight Phthalate Esters (PEs), six Polychlorinated Biphenyls (PCBs) and two Alkylphenols (APs) were quantitative analyzed in a single run. The best parameters for extraction were determined, including fiber type, sample volume, salinity and extraction time and temperature. In the optimized procedure, 15 ml of water sample was extracted using a 100 µm PDMS fiber in a 20 ml vial and adding 3 g of NaCl (final NaCl concentration of 20%) during 40 min at 80°C (with 10 min of previous equilibration time). A desorption time of 15 min was shown to eliminate carry-over. The method showed good linearity between 0.01 and 10 $\mu g L^{-1}$ (r^2 from 0.987-0.999). Good precision (63-123%) and accuracy were achieved (1.1-21%). The Methodological Detection Limits (MDL) ranged from 0.00001-0.01364 $\mu g\ L^{-1}$. The method was successfully applied to real samples collected at Ensenada (Mexico). The proposed method represents an effectively and valuable tool for application in environmental water monitoring programs.

Keywords: HS-SPME-GC-MS/MS; Multiresidual analysis; Organic xenobiotics; Environmental waters; Water monitoring

Introduction

Xenobiotics cover a wide range of organic chemicals not present in nature without prior synthesis by humans or at least not present at worryingly high concentrations without human activities. Xenobiotics are introduced to the environment mainly from industrial, agricultural and domestic activities. A multitude of xenobiotics with variable origins, applications, structures, and properties has increasingly attracted attention during the past decade [1]. Aquatic environment including lakes, rivers, seas [2] and groundwater [3,4], is the environmental compartment more affected by the daily input of those organic chemicals. Xenobiotics, called also as Organic Micropollutants (OMPs) can alter aquatic organisms at nanogram to milligram per liter levels [5,6] producing endocrine disruption and neurotoxicity [7]. Some OMPS are bioaccumulative [8] and could reach the higher levels of trophic chain, like humans [9,10]. In the other hand, ground and surface waters are used as a source of drinking water [11], as well as for agricultural, recreational, commercial and industrial activities [12-14]. Consequently, water pollution can be a threat to the ecosystem and the public health. Several xenobiotics have been detected in the aquatic environment at trace levels including APs [3,15,16], PAHs, PCBs [15,17], PEs [3,15,18], among others. The groups of PAHs are known or suspect carcinogens [19,20]. APs and plasticizers like BPA and PEs are ubiquitous environmental contaminants that posse possible estrogenic properties [18,21-23]. PCBs are banned for productions and utilization and can cause toxic responses include dermal toxicity, immunotoxicity, carcinogenicity, and adverse effects on reproduction, development, and endocrine functions [24].

In developing countries such as in México, environmental issues are being relevant and are considered into their National Development Plans [25]. To assess the environmental impacts of industrial and domestic settlements it is necessary establish monitoring programs. There are required tools capable to give a minute picture of the state of the water bodies. Multiresidual methods can provide information of multiple compounds simultaneously. They allow the simultaneous identification and quantification of a wide range of organic contaminants in a single analysis [6,26,27]. Traditional extraction methodologies comprise Solid Phase Extraction (SPE) or Liquid-Liquid Extraction (LLE). SPE and analysis by GS coupled to MS (GC-MS) [13] or to MS in tandem (GC-MS/MS) [6] was previously used for the simultaneous analysis of PAHs, APs, PEs and PCBs in environmental waters. One alternative to traditional methodologies is SPME.

SPME is a sample preparation technique where no organic solvents are required. It presents a number of advantages over LLE and SPE. The technique decreases the steps for sample preparation and has become an accepted method for the determination of volatile and semi-volatile substances. It is a pretreatment methodology very simple, fast, easily, automated and inexpensive. Also only small volumes of samples are needed. It can be coupled directly to GC [28,29]. SPME integrates sampling, extraction, purification, concentration and injection into one procedure [30]. SPME can be done by Direct

Immersion (DI) or by Headspace (HS), exposing the fiber to the gas phase equilibrated with the sample. Although DI-SPME seems to be more appropriated for semi-volatile compounds [31], HS-SPME was successfully used for dirty or complex matrixes [30,31]. Usage of HS-SPME protects the fiber from adverse effects caused by non-volatile and high molecular weights substances present in the sample matrix [30], and with this, the fiber can last up to 150 extractions.

In our knowledge, there are not reported methodologies using HS-SPME-GC-MS for the simultaneous analysis of PAHs, APs, PEs and PCBs. Using commercial fibers, only a few published methodologies were found for the single analysis in environmental waters of PAHs [32-35] and of PCBs [35-37] and the simultaneous analysis of PAHs and PCBs [38,39] and of APs and PEs [40].

In this study a method based in HS-SPME and GC-MS/MS for the identification and quantification of 34 target xenobiotics belonging to different chemical families has been carried out. This method was applied for the analysis of trace xenobiotics in environmental waters including from rain, sea and groundwater to evaluate its performance. For water monitoring of a large variety of xenobiotics and baseline establishment, a cost-effective and solvent-less screening technique was developed. All the analysis were done in the facilities of the Specialized Laboratories System of the Mexican Center for Innovation in Geothermal Energy (SLS-CeMIEGeo).

Experimental

Chemical and reagents

Eighteen PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, 2-methylnaphthalene, 1-methylnaphtalene, Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-cd)pyrene, Dibenzo(a,h)anthracene and Benzo(g,h,i)perylene); eight PEs (Dimethyl phthalate, Diethyl phthalate, Dibutyl phthalate, Bis(4-methyl-2-pentyl)phthalate, Dipentyl phthalate, Dihexyl phthalate, Butyl benzyl phthalate and Dicyclohexyl phthalate); six PCBs (congeners 28, 52, 101, 138, 153 and 180); two APs (Octylphenol and Nonylphenol) and finally as internal standards; Six deuterated PAHs (Naphthalene-d8, Acenaphthylene-d8, Phenanthrene-d10, Fluoranthene-d10, Pyrene-d10, Benzo(a)pyrene-d12); four deuterated PEs (Dimethyl phthalate-d4, Dibutyl phthalate-d4, Dicyclohexyl phthalate-d4, Bis(2-ethylhexyl)phthalate-d4), Tetrachloro-m-xylene and PCB 209 were analyzed (Table 1). Non-methylated PAHs, PEs mix and deuterated PEs were purchased from AccuStandard, Inc. (New Haven, USA); methylated PAHs were purchased from Chem Service (West Chester PA, USA); PAH surrogate standard mix was purchased from Cambridge Isotope Laboratories (Andover, USA); PCBs congener mix, Alkylphenol mix, Tetrachloro-m-xylene and PCB 209 were purchased from Supelco-Sigma (Bellefonte, USA). Sodium chloride (NaCl) (ACS reagent >99%) and iso-octane (GC grade) were supplied from Merck (Darmstadt, Germany). Helium gas (99.9999%) and Nitrogen gas (99.9995%) were supplied from Praxair México (Baja California, México). Working solutions (10 and 100 μg mL^{-1}) of target and surrogate standards were prepared in iso-octane and stored under refrigeration (2-4°C). Four commercial SPME fibers including 30 and 100 μm Polydimethylsiloxane (PDMS), 65 μm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) and 75 μm Carboxen/Polydimethylsiloxane (Car/PDMS) were purchased from Supelco.

Time seg.	RT (min)	Compound	Q Transition	Col. E. eV	q Transition	Col. E. eV	q/Q ratio (%)	Internal standard
	6.0	**Naphthalene d_8**	136.0>108.0	15	136.0>84.0	20	65.2	-
	6.2	Naphthalene	128.0>102.0	15	128.0>78.0	20	97.1	Naphthalene d_8
	9.7	**Acenaphthylene d_8**	160.0>158.0	15	160.0>132.0	25	58.8	-
	9.8	Acenaphthylene	152.0>151.0	15	152.0>126.0	25	34.5	Acenaphthylene d_8
	9.9	**Dimethyl phthalate d_4**	167.0>96.0	20	167.0>81.0	35	34.3	-
	10	Dimethyl phthalate	163.0>77.0	20	163.0>135.0	10	16.9	Dimethyl phthalate d_4
1	10.2	Acenaphthene	154.0>153.0	5	154.0>152.0	15	16.9	Acenaphthylene d_8
	11.4	Fluorene	166.0>165.0	5	166.0>164.0	30	29.4	Acenaphthylene d_8
	11.6	Octylphenol	135.0>107.0	35	135.0>95.0	35	8	Phenanthrene d_{10}
	11.6	Diethyl phthalate	149.0>65.0	20	149.0>93.0	15	71.4	Dimethyl phthalate d_4
	11.8	**Tetrachloro-m-xylene**	206.8>136.0	25	243.7>209.0	30	49.5	-
	12.7-13.7	Nonylphenol (isomer mix)	135.0>107.0	35	135.0>95.0	35	7.8	Phenanthrene d_{10}
	13.9	**Phenanthrene d_{10}**	188.0>160.0	20	188.0>184.0	30	83.3	-
	13.9	Phenanthrene	178.0>152.0	15	178.0>176.0	25	27.8	Phenanthrene d_{10}
2	14.1	Anthracene	178.0>152.0	15	178.0>176.0	25	66.7	Phenanthrene d_{10}

	15.5	PCB 28	255.7>186.0	30	257.7>186.0	35	43.5	Tetrachloro-m-xylene
	15.9	2-Methylnaphthalene	192.0>191.0	5	191.0>189.0	25	94.9	Phenanthrene d_{10}
	16.3	1-Methylnaphtalene	192.0>191.0	5	191.0>189.0	25	82.6	Phenanthrene d_{10}
	16.7	PCB 52	291.7>222.0	35	219.8>150.1	40	96	Tetrachloro-m-xylene
	17	**Dibuthyl phthalate d_4**	153.0>69.0	25	153.0>125.0	15	35.7	-
3	17	Dibutyl phthalate	149.0>65.0	20	149.0>93.0	15	98.2	Dibuthyl phthalate d_4
	18.5	**Fluoranthene d_{10}**	212.0>210.0	20	212.0>208.0	30	90.9	-
	18.6	Fluoranthene	202.0>201.0	15	202.0>200.0	30	83.3	Fluoranthene d_{10}
	19.0-19.2	Bis(4-methyl-2-pentyl)phthalate	149.0>65.0	25	149.0>93.0	15	55.6	Dibuthyl phthalate d_4
	19.4	**Pyrene d_{10}**	212.0>210.0	20	212.0>208.0	30	90.9	-
	19.5	Pyrene	202.0>201.0	15	202.0>200.0	30	90.9	Pyrene d_{10}
	19.7	PCB 101	325.6>256.0	40	253.7>184.0	40	83.3	Tetrachloro-m-xylene
4	20.3	Dipentyl phthalate	149.0>65.0	20	149.0>93.0	15	58.8	Dibuthyl phthalate d_4
	22.7	PCB 138	359.6>290.0	35	289.7>218.1	45	40	Tetrachloro-m-xylene
	23.5	Dihexyl phthalate	251.0>149.0	5	251.0>93.0	45	15.4	Dibuthyl phthalate d_4
	23.5	Butyl Benzyl phthalate	206.0>149.0	5	206.0>121.0	25	11.5	Dibuthyl phthalate d_4
	23.7	PCB 153	359.6>290.0	35	289.7>218.1	45	45.5	PCB 209
	24.9	Benz(a)anthracene	228.0>227.0	15	228.0>226.0	30	23.8	Pyrene d_{10}
	25.2	Chrysene	228.0>227.0	15	228.0>226.0	30	38.5	Pyrene d_{10}
	26	PCB 180	393.6>324.0	35	323.6>254.0	40	52.6	PCB 209
	26.1	**Dicyclohexyl phthalate d_4**	153.0>69.0	25	153.0>125.0	15	33.3	-
5	26.2	Dicyclohexyl phthalate	149.0>93.0	15	149.0>65.0	20	55.6	Dicyclohexyl phthalate d_4
	29.6	Benzo(b)fluoranthene	252.0>250.0	30	126.0>112.0	20	19.6	Benzo(a)pyrene d_{12}
	29.7	Benzo(k)fluoranthene	252.0>250.0	30	126.0>112.0	20	20.8	Benzo(a)pyrene d_{12}
	30.7	**Benzo(a)pyrene d_{12}**	264.0>260.0	30	264.0>236.0	30	26.3	-
	30.8	Benzo(a)pyrene	252.0>250.0	30	126.0>112.0	20	20.8	Benzo(a)pyrene d_{12}
	31.4	**PCB 209**	497.5>428.0	40	427.5>358.0	40	33.3	-
	34.9	Indeno(1,2,3-cd)pyrene	276.0>274.0	30	276.0>275.0	10	28.6	Benzo(a)pyrene d_{12}
	35.1	Dibenzo(a,h)anthracene	278.0>276.0	30	279.0>277.0	30	21.7	Benzo(a)pyrene d_{12}
	35.6	**Benzo(g,h,i)perylene d_{12}**	288.0>286.0	20	288.0>284.0	30	30.3	-
6	35.7	Benzo(g,h,i)perylene	276.0>274.0	30	276.0>275.0	10	10.5	Benzo(a)pyrene d_{12}

Table 1: Optimized parameters for the target compounds including retention time (min), quantification (Q) and qualification (q) transitions, collision energy (in eV) and the Q/q ratio and internal standard used for quantification. Compounds in **bold** are the surrogate standards.

Sample location and sampling

Rainwater samples were collected on an event basis at the roof-top of the Mexican Center of Innovation in Geothermal Energy (CeMIE-Geo) building, at Ensenada, México. Two samples were collected on January 13, 2017 using a glass funnel. Samples were stored in a pre-cleaned 500 ml amber glass bottles sealed with a screw cap with PTFE liners and stored at -20°C until analysis.

Surface coastal seawater samples were collected at the Autonomous University of Baja California beach at Ensenada, México, on January

09, 2017 using pre-cleaned 500 ml amber glass bottles sealed with a screw cap with PTFE liners and stored at -20°C until analysis.

Groundwater samples were collected from wells from the Municipality of Ensenada, on October 13, 2016 using pre-cleaned 250 ml amber glass bottles sealed with a screw cap with PTFE liners, transported to CeMIE-Geo, Ensenada in a cooler at 4°C, and finally stored at -20°C until analysis.

All amber glass bottles and the glass funnel used in collection and storage of samples have undergone through cleaning prior usage: washed with non-ionic detergent at 20%, rinsed with tap water, followed with deionized water and milli-Q water; rinsed with acetone and finally baked at 450°C for 4 hrs.

Automated headspace-solid phase microextraction procedure

An Agilent's GC-Sampler-80 auto-sampler with SMPE agitator attachment (CTC Analytics, Zwingen, Switzerland) were used for agitation and heating of the samples as well as injection into the GC-MS/MS. Also a needle-heater attachment (CTC Analytics) was used for the cleaning of the fiber. During extraction and injection, a fiber holder was used to grab the SPME fiber. A volume of 10 or 15 ml of water containing surrogate at 0.3 μg L^{-1} was placed in a 20 ml vial adding 0, 5, 10 or 20% of NaCl and it was sealed with a PTFE septum (with a magnetic cap). Four different commercial SPME fibers were tested for the extraction of the target analytes: PDMS 100 μm, PDMS 30 μm, PDMS/Car and PDMS/DVB. The fiber was conditioned prior to the first use with the temperature and time recommended by the manufacturer. Three different temperatures and 3 extraction times were evaluated: 40, 60 and 80°C and 20, 40 and 60 minutes. Before the extraction, the vial was preheated for 10 minutes at the evaluated temperature and stirred at 750 rpm; then the stirring was automatically fixed at 250 rpm and the fiber was inserted into the vial in the headspace during the tested time. After the sorption process, the SPME fiber was immediately desorbed at the manufacturer's recommended temperature for 5 minutes on the injection port and placed 10 minutes more, into the needle-heater.

GC instrumentation

Chromatographic analyses were carried out using a 7890B Agilent GC chromatographic system (Palo Alto, USA) coupled to a 7000C Agilent triple quadrupole (QqQ) mass spectrometer system. A DB-5MSUI column (30 m length × 250 μm i.d. × 0.25 mm film thickness) from Agilent was used for chromatographic separation. The oven temperature was started at 80°C, held for 2 minutes; then increased at 10°C min^{-1} up to 180°C, held for 2 minutes; increased at 5°C min^{-1} up to 290°C and held for 7 min. The Multimode Injector port (MMI) was equipped with a 0.75 mm ID straight liner and a Merlin seal, both from Agilent and operated in splitless mode at the desorption temperature, following the SPME fiber's manufacturer recommendations. Split valve was closed for 5 min and then, a split flow of 100 ml min^{-1} was applied. A constant flow of Helium at 1.1 ml min^{-1} was used as carrier gas. Transfer line and ionization source temperatures were 290 and 270°C respectively. Nitrogen was used as collision gas at 1.25 ml min^{-1}.

Ionization was made by Electron Impact (EI) +70 eV. For all compounds two MS/MS transitions were optimized in Selected Reaction Monitoring (SRM) mode; one transition was used for Quantification (Q) and the other for identification (q) (Table 1). A solvent delay of 5 min was set to protect the filament from oxidation. Quantification was done with the internal standard method. Table 1 shows the chromatographic and mass spectrum parameters used for the identification and quantification of each target compound.

Results

HS-SPME optimization

Parameters affecting the PAHs, APs, PEs and PCBs recoveries of HS-SPME were investigated using milli-Q grade water free of endocrine disruptors, spiked with known concentrations of the 34 xenobiotics. The aim of this study was to optimize HS-SPME to obtain high extraction efficiency. The parameters predicted to affect the extraction are: type of fiber, heating temperature, incubation time, agitation speed, ion strength and sample volume [30,32,35,41]. In the agitation/heating attachment, the agitation speed during the extraction was fixed by default at 250 rpm, so this parameter could not be changed. The optimization was carried out by comparing the chromatographic areas of the compounds analyzed at the different evaluated conditions. The HS-SPME initial conditions were as follow: 10 ml of sample contained into a 20 ml PTFE/silicone magnetic screw glass vial; no NaCl was added; target compounds were spiked to obtain a concentration of 0.4 μg L^{-1}; the temperature of incubation was maintained in 60°C. With the aim of equilibrate the gas phase and the sample, vials were preheated for 10 min; then, the SPME fiber was exposed 30 min to the HS above the aqueous phase. After extraction, the fiber was thermally desorbed into the GC injection port. For convention, 270°C was chosen.

SPME fiber selection: The choice of the SPME fiber was done considering that different chemical families should be analyzed in a single run. Three different commercial fiber coatings (PDMS, PDMS/DVB and Car/PDMS) were evaluated. Also, two PDMS thicknesses were tested (30 μm and 100 μm). Initial conditions were as mentioned above. Figure 1 shows the relative extraction efficiencies of the 19 PAHs, 6 PCBs, 8 PEs and 2 APs, expressed by the sum of peaks areas grouped by family. Higher peak areas were obtained with PDMS 100 μm fiber for all families. Therefore, this fiber was considered most suitable for this study and it was selected for further experiments.

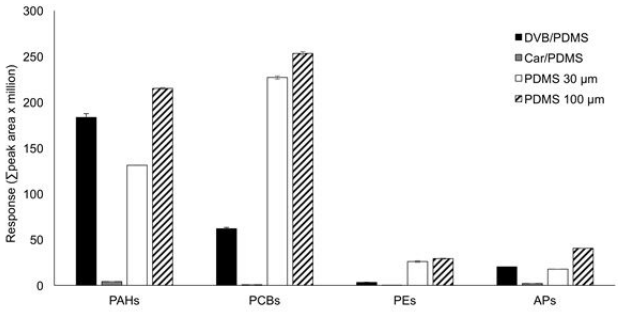

Figure 1: Comparison of the response of the studied compounds at 0.4 μg L^{-1} without salting (n=3), extracted in HS-SPME mode at 60°C for 20 minutes, using four different fibers (DVB/PDMS, Car/PDMS, PDMS 30 μm and PDMS 100 μm).

In order to ensure the complete desorption of the heavier compounds, and avoid the carry-over effect, a higher temperature than

the recommended by the supplier, was selected. Thus, fifteen minutes at 290°C was enough for the complete desorption of the target compounds. In previously works [30], was proved that with the usage of a similar temperature for desorbing the fiber, more than 100 injections were successfully injected without loss of efficiency.

HS-SPME extraction time and temperature: The maximum amount of analyte that can be extracted by the fiber is achieved at the equilibrium time [34]. Less volatile analyte require a long equilibrium time. Nevertheless, in order to maximize sample output, reasonable extraction times were evaluated. Besides, temperature plays a significant role in SPME method sensitivity as it increases vapor pressure for volatile analyte in the head space. However, higher temperatures might also create a less favorable coating-headspace (air) partition [41]. Optimization of SPME time and temperature was traditionally considered as independent parameters [30,35,41]. In this study, the effect of temperature and time were simultaneously studied by exposing the fiber in HS mode at different temperatures (40, 60 and 80°C) and different times (20, 40 and 60 min). Conditions were the same as above, using a PDMS 100 µm fiber. Figure 2 shows the effect of extraction temperature and time on the areas of the representative families of target compounds. For PAHs the maximum responses were obtained with 60°C and 60 min; for PCBs and for APs, 60°C and 40 min; for PEs, 80°C and 40 min. Indeno(1,2,3-cd)pyrene, Dibenzo(a,h)anthracene and Benzo(g,h,i)perylene were only extracted at 80°C. Given the variety of the target analyte in terms of volatility, it was necessary to reach a compromise solution to obtain, using only one temperature and time, the best possible results for all compounds. Thus, 80°C and 40 min was selected as the best parameters to determine the mixture of 34 compounds. Using this temperature and time, areas were duplicated in almost all cases, compared with the initial conditions.

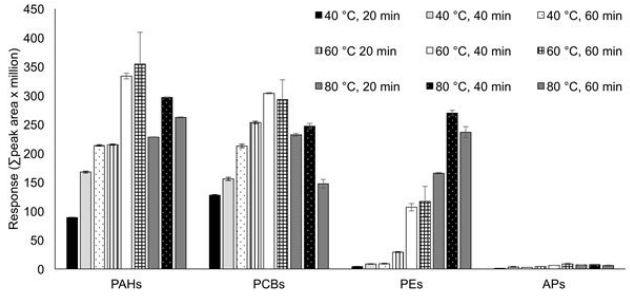

Figure 2: Comparison of the response of the studied compounds at 0.4 µg L^{-1} without salting (n=3), extracted in HS-SPME mode at 40, 60 and 80°C for 20, 40 and 60 minutes, using a PDMS 100 µm fiber.

Sample volume: In head space extraction, the analyte is partitioned among three phases: the original sample, the headspace and the SPME sorbent. Headspace is influenced by the sample volume. The efficiency of the extraction depends on the volume of the headspace and it should be as small as possible to prevent the excessive dilution of analyte in this phase [42]. In this study, two volumes were evaluated: 10 ml and 15 ml in a 20 ml headspace vial. Figure 3 shows the effect of the sample volume on the areas of the target compounds. For all families, areas were duplicated using 15 ml of sample. So, 15 ml was selected as the sample volume. The use of larger volumes is not feasible, because would not provide enough space for the needle and the SPME fiber.

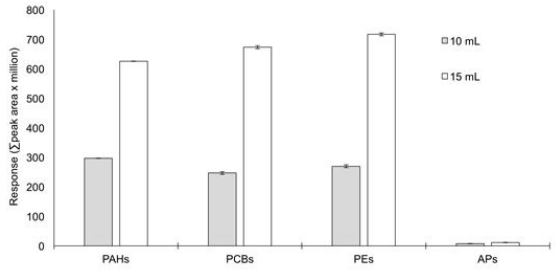

Figure 3: Comparison of the response of the studied compounds at 0.4 µg L^{-1} without salting (n=3), extracted in HS-SPME mode using 100 µm PDMS fiber at 80°C for 40 minutes evaluating two different sample volume: 10 ml and 15 ml.

Ionic strength: Salting out (addition of salt) usually has a positive effect on the extraction recoveries using HS-SPME. The addition of salt increases the ionic strength of the sample, which reduces the solubility of the analyte; and favoring the transfer of the analyte from the aqueous, to the gaseous phase [4]. In this study, the ionic strength had a positive effect on the extraction of all the families of target compounds, especially on the APs and PEs (the most polar compounds studied). Figure 4 shows the behavior of the areas response of the target families when NaCl is added from 0, to 20% (0, 5, 10 and 20%). Salting out, using 20% of NaCl, enhanced 28-fold the areas response of APs and 9-fold of PEs; where the other method changes were not as significant as this. For the PAHs the increment in areas was 3-fold and for PCBs, 1.3-fold. In consequence, 20% was selected for salting out because the results showed highest response. The option of using DI was initially evaluated, but DI is not practicable when salt is used as a matrix modifier as it causes faster degradation of the coating [4].

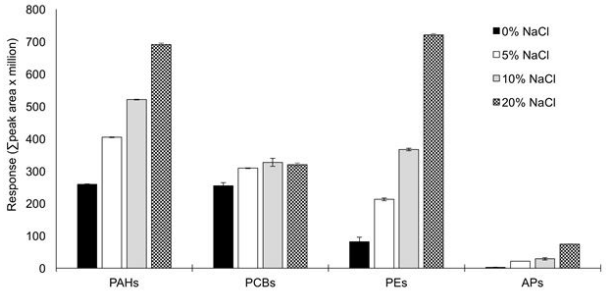

Figure 4: Comparison of the response of studied compounds at 0.4 µg L^{-1} (n=3) extracted in HS-SPME mode using 100 µm PDMS fiber at 80°C for 40 minutes using four different salting concentrations: 0, 5, 10 and 20% of NaCl.

Performance evaluation of the proposed method

According to European Decision 2002/657/EC, to confirm the peak identity in samples, 4 identifications points must be obtained. Retention time and two SRM transitions were used and also the Q/q ratio (%) criterion considering: when Q/q was >50%, a tolerance of ± 50% is allowed; Q/q>20 to 50%, a tolerance of ± 25; Q/q>10 to 20%, a

tolerance of ± 30% and Q/q ≤ 10%, a tolerance of ± 50% (Table 1). Figures 5a-5d display as example the transitions of one compounds of each chemical family studied, showing their retention time, Q and q transitions and the Q/q ratio, and expressed in percentage, the tolerance.

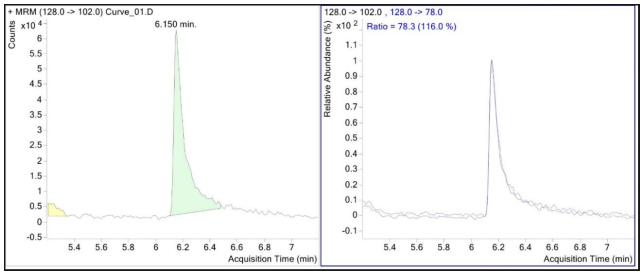

Figure 5a: SRM transitions, showing their Q/q ratio tolerance-Naphthalene.

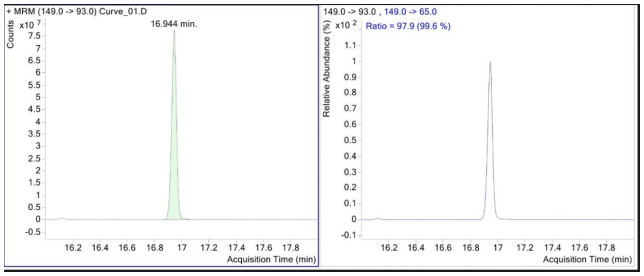

Figure 5b: SRM transitions, showing their Q/q ratio tolerance-Dibutyl phthalate.

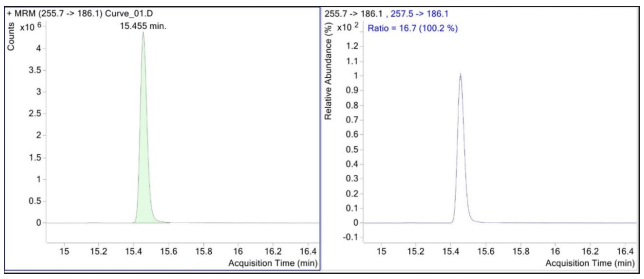

Figure 5c: SRM transitions, showing their Q/q ratio tolerance-PCB 28.

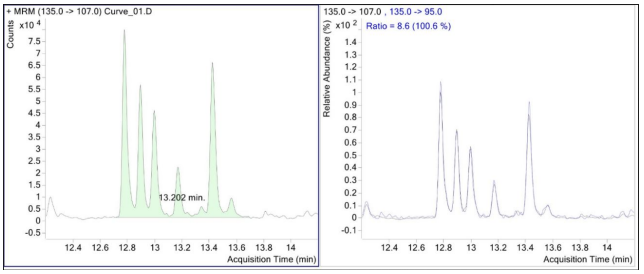

Figure 5d: SRM transitions, showing their Q/q ratio tolerance-Nonylphenol.

Linearity of the method was studied using milli-Q water spiked with target compounds in a concentration range from 0.01 to 100 µg L^{-1} with 7 calibration levels, and 0.3 µg L^{-1} of surrogate standards. The linear range was from 0.01 to 100 µg L^{-1}, except for PCBs (0.01 to 10 µg L^{-1}). Good linearity was exhibited for all target compounds at the tested concentrations ranges, with coefficients of determination (r^2) from 0.987-0.99.

To evaluate the accuracy, analytical recoveries of spiked milli-Q water were determined (n=6) at 3 levels of concentration (0.4, 1 and 2 µg L^{-1}). For concentrations below 10 µg L^{-1}, acceptable recoveries are considered from 60 to 115% [43-46]. In this study good recoveries were obtained (63-114%), except for phthalates in the lowest range.

Repeatability was calculated as RSD (%) of concentrations using 6 replicates analyzed the same day by the same analyst and the same equipment, using 3 different levels of concentration. According to AOAC Peer Verified Methods Program [19,43], for concentrations below 10 µg L^{-1}, acceptable RSD must be lower than 21%. For all cases, good RSD values were obtained (1.1 to 21%). Reproducibility was also determined in different days of same week (n=6) with a concentration of 1 µg L^{-1}, with similar variations than repeatability (data not shown).

The MDL and Method Quantification Limits (MQL) were estimated as 3 times and 10 times (respectively) the signal-to-noise-ratio of the lowest concentration of the calibration curve. MDL ranged from 0.00001 (PCB 101) to 0.01364 µg L^{-1} (nonylphenol). MQL ranged from 0.00002 (PCB 101) to 0.04545 µg L^{-1} (nonylphenol).

Due to the matrix effect that often affects the SPME technique, quantitative measurements in real samples were performed applying the standard addition method. For that reason, three replicates of rain, ground and sea waters were spiked with 10 µg L^{-1} of target compounds. The obtained values were found to be quantitative (>65%).

Table 2 summarizes the method accuracy (recoveries), precision (%RSD, n=6), MDL and MQL and the linearity (r^2).

	0.5 µg L^{-1} (n=6)		1 µg L^{-1} (n=6)		2 µg L^{-1} (n=6)		MDLµg L^{-1}	MQLµg L^{-1}	r^2
Compound	**Rec.(%)**	**RSD(%)**	**Rec.(%)**	**RSD(%)**	**Rec.(%)**	**RSD(%)**			
Polyaromatic hydrocarbons									
Napthalene	96	8.4	87	11	88	10	0.0022	0.0074	0.998

Acenaphtylene	93	9.6	112	17	95	7.2	0.0022	0.0074	0.99
Acenaphthene	88	12	112	16	108	11	0.0021	0.0068	0.993
Fluorene	83	4.6	101	5.9	108	8.9	0.0006	0.002	0.993
Phenanthrene	99	14	97	8.1	96	11	0.0005	0.0016	0.999
Anthracene	92	3.5	82	3.3	85	2.7	0.0018	0.0059	0.995
2-methylnaphthalene	78	3.5	87	6.3	90	7.9	0.0001	0.0003	0.999
1-methylnaphthalene	72	5.7	86	6.6	90	6	0.0011	0.0036	0.999
Fluoranthene	91	3.4	93	2.9	90	3.8	0.0002	0.0006	0.997
Pyrene	96	5.7	96	2	92	5.4	0.0004	0.0012	0.998
Benz(a)anthracene	65	15	75	4.7	81	18	0.0005	0.0016	0.999
Chrysene	67	13	79	6.4	86	19	0.0004	0.0015	0.998
Benzo(b)fluoranthene	74	12	75	16	79	18	0.0025	0.0084	0.997
Benzo(k)fluoranthene	71	9.3	86	9.4	108	9.3	0.001	0.0034	0.99
Benzo(a)pyrene	77	5.7	89	8.6	113	7.1	0.0028	0.0093	0.991
Indeno(cd)pyrene	109	1.7	110	4.7	83	14	0.0011	0.0036	0.996
Dibenzo(ah)anthracene	114	6.2	106	9.9	105	7	0.0006	0.0019	0.993
Benzo(ghi)perylene	108	20	112	13	109	15	0.001	0.0034	0.998
Polychlorobiphenyls									
PCB 28	93	6.9	95	15	101	12	0.00002	0.00008	0.991
PCB 52	92	7.9	109	13	105	12	0.00001	0.00004	0.994
PCB 101	92	5.6	108	14	95	12	0.00001	0.00002	0.991
PCB 138	91	13	106	11	108	11	0.00001	0.00004	0.999
PCB 153	95	10	108	11	106	12	0.00001	0.00002	0.997
PCB 180	102	12	104	16	106	12	0.00001	0.00002	0.992
Phthalate esters									
Dimethyl phthalate	123	21	114	15	110	15	0.0018	0.006	0.99
Diethyl phthalate	119	18	108	10	113	17	0.0001	0.0002	0.987
Dibuthyl phthalate	99	5.6	85	3.2	90	6.5	0.0001	0.0002	0.993
Bis(4-methyl-2-pentyl) phthalate	83	8.2	84	3.5	109	7.2	0.0002	0.0006	0.995
Dipentyl phthalate	76	11	79	11	100	4.7	0.0001	0.0002	0.998
Dihexyl phthalate	116	10	92	7.8	98	6.1	0.0002	0.0001	0.991
Butylbenzyl phthalate	123	1.5	84	21	99	7.7	0.0002	0.0007	0.995
Dicyclohexyl phthalate	77	2.4	101	12	103	8.8	0.0002	0.0005	0.998
Alkylphenols									
Octylphenol	73	6.2	73	9.2	81	3.5	0.006	0.02	0.999

Nonylphenol (isomer mix)	63	5.2	71	9	85	1.1	0.014	0.045	0.998

Table 2: Figures of merit of the HS-SPME-GC-MS/MS method developed.

If compared with other methods directed to the same target analyte and same matrixes, the combination of HS-SPME and GC-MS/MS as studied here showed similar or better performance in terms of detection limits, precision, accuracy and linearity (Table 3).

Compound family	Matrix studied	SPME mode	r^2	MDL (µg L^{-1})	Accuracy (Recov. %)	Precision (RSD %)	Observations	Ref.
PAHs	Rain water	DI	0.991-0.996	0.001-0.041	72-109	May-16	16 EPA PAHs were analyzed. Method performance was determined in Mili-Q water using a 100 µm PDMS fiber.	[34]
	Sea and sediment pore water	DI	0.9002-0.9999	0.0001-0.0017	76-107	Apr-23	16 EPA PAHs were analyzed. Method performance was determined in seawater using a 100 µm PDMS fiber.	[19]
	Groundwater	HS	0.980-0.998	0.09-0.24	2.6-56.1	Dec-03	16 EPA PAHs were analyzed. Method performance was determined in Mili-Q water using a 100 µm PDMS fiber.	[44]
	Rain, sea and ground waters	HS	>0.9901	0.0001-0.064	71-114	Feb-20		This study
PEs	Groundwater	DI	>0.99	0.0001-0.0016	Not specified	<5	Method performance was determined in Mili-Q water using a 100 µm PDMS fiber.	[21]
	Rain, sea, and ground waters	HS	>0.993	0.0003-0.0011	76-123	2.4-21		This study
PCBs	Seawater	HS	0.974-0.998	0.0003-0.0075	69-99	3.9-15	Congeners 1, 5, 29, 47, 98, 154, 171 and 201 were analyzed. Samples were treated with $KMNO_4$. Method performance was determined in Mili-Q water using a 7 µm PDMS fiber.	[45]
	Rain, sea, and ground waters	HS	0.991-0.999	0.0001-0.0006	91-109	5.6-15		This study
APs	Well, drinking, and pool waters	DI	0.993-0.998	0.38-0.75	82.6-94.4	3.9	Octylphenol and nonylphenol were analyzed. Method performance was determined in Mili-Q water using a 30 µm PDMS fiber.	[46]
		HS	0.9979-0.9993	0.001-0.030	63-73	1.1-9.2		This study

Table 3: Comparison of the performance of some reported methods for the target compound extraction and analysis using commercial fibers.

Analysis of real samples

The low detection limits of the developed methodology suggested that it is satisfactory for water monitoring. The optimized methodology was applied to check the presence of target compounds in some real environmental water samples, including rain, tap, sea and river waters. The objective was to show the applicability of the method developed rather than performing a detailed comparative study of target compounds pollution in the samples.

Three samples of rain water, three from seawater and five from groundwater were evaluated, and their concentrations were calculated by internal standard method from a 15 ml volume, salted with 3 g of NaCl (final concentration of NaCl, 20%). When it was necessary, a dilution was made to fit concentration within the range of the calibration curve. The obtained results are shown in Table 4. PAHs and PEs were the most ubiquitous, detected in all samples. APs and PCBs were detected in sea and groundwater. In rainwater PAHs were the most abundant xenobiotics (Σ PAHs=0.5198-176 µg L^{-1}), followed by PEs (Σ PEs=0.895-36.87 µg L^{-1}). In seawater APs were the most abundant (Σ APs=0.0917-120 µg L^{-1}), followed by PEs (Σ PEs=0.882-54.0 µg L^{-1}), PAHs (Σ PAHs=1.28-47.3 µg L^{-1}) and finally by PCBs (Σ PCBs=0.0853-0.440 µg L^{-1}). In groundwater PEs were the most abundant (Σ PEs=86.0-639 µg L-1), followed by PAHs (Σ PAHs=2.31-43.2 µg L^{-1}), APs (Σ APs=0.0205-6.86 µg L^{-1}) and finally by PCBs (Σ PCBs=0.0016-6.86 µg L^{-1}).

Compound	Rain 1	Rain 2	Rain 3	Sea 1	Sea 2	Sea 3	Ground 1	Ground 2	Ground 3	Ground 4	Ground 5

Polycyclic aromatic hydrocarbons											
Naphthalene	0.408	0.254	0.0336	0.111	4.86	2.49	7.81	17.85	0.605	2.24	2.62
Acenaphthylene	ND	ND	ND	0.22	0.163	0.192	1.49	ND	ND	ND	ND
Acenaphthene	ND	ND	ND	0.234	0.196	0.215	1.63	ND	0.0435	0.0383	ND
Fluorene	0.0344	0.0511	ND	0.0655	27	13.5	3.26	0.51	0.501	0.009	0.0074
Phenanthrene	0.463	0.0189	ND	0.0527	8.06	4.05	1.75	1.01	0.143	ND	0.01
Anthracene	1.25	ND	0.1328	0.048	1.52	0.785	2.45	2.06	0.0878	ND	ND
2-methylnaphthalene	0.143	0.0055	ND	0.0461	0.482	0.264	1.01	0.369	0.0943	ND	0.0016
1-methylnaphthalene	0.169	ND	ND	0.0483	1.51	0.784	0.953	0.409	0.0228	ND	ND
Fluoranthene	0.0385	0.0035	ND	0.0438	0.0369	0.0404	1.73	1.09	0.0355	ND	ND
Pyrene	0.0472	0.0059	ND	0.0437	0.0729	0.0583	1.64	0.908	0.0466	ND	ND
Benz(a)anthracene	1.53	0.0056	6.51	0.048	0.0823	0.0651	1.67	1.1	0.115	ND	0.0065
Chrysene	1.81	0.0517	5.83	0.0489	0.245	0.147	3.55	1.22	0.201	ND	0.0159
Benzo(b)fluoranthene	5.35	0.0428	61.4	0.0503	0.641	0.346	4.52	2.29	ND	ND	ND
Benzo(k)fluoranthene	1.13	0.044	32.4	0.0727	1.52	0.798	8.21	0.76	0.484	ND	0.0152
Benzo(a)pyrene	8.8	ND	69.7	0.0434	0.195	0.12	1.05	ND	ND	ND	ND
Indeno(cd)pyrene	ND	ND	ND	0.0141	0.25	0.132	0.475	0.341	0.0798	ND	ND
Dibenzo(ah)anthracene	ND	0.0096	ND	0.0206	0.188	0.105	ND	ND	0.331	0.0101	0.0099
Benzo(ghi)perylene	ND	0.0272	ND	0.0689	0.235	0.152	ND	ND	1.11	0.0073	0.0256
Polychlorinated biphenyls											
PCB 28	ND	ND	ND	0.0853	0.0105	0.0474	ND	ND	0.0105	ND	ND
PCB 52	ND	ND	ND	ND	0.0128	0.0574	ND	ND	0.0081	ND	ND
PCB 101	ND	ND	ND	ND	0.0366	0.0749	ND	ND	0.0164	ND	ND
PCB 138	ND	ND	ND	ND	0.0645	0.0917	1.08	0.658	0.0231	ND	ND
PCB 153	ND	ND	ND	ND	0.0647	0.0861	1.85	1.43	0.0233	ND	ND
PCB 180	ND	ND	ND	ND	0.0724	0.0825	3.93	2.93	0.0291	0.0016	0.0017
Phthalate esters											
Dimethyl phthalate	0.284	36.6	0.206	0.391	5.28	2.87	117	119	83.7	6.79	8.71
Diethyl phthalate	0.578	0.0147	0.307	0.061	0.117	0.0895	15.6	17.8	0.378	0.0721	0.0848
Dibuthyl phthalate	0.359	0.008	0.206	0.222	45.8	22.9	96.3	108	553	78.3	97.2
Bis(4-methyl-2-pentyl) phthalate	0.0272	ND	ND	0.0475	0.168	0.108	2.47	2.6	0.167	0.023	0.0436
Dipentyl phthalate	0.233	0.0246	0.176	0.0451	0.0382	0.0416	2.11	1.92	0.0431	0.0047	0.0348
Dihexyl phthalate	ND	0.0476	ND	0.0425	0.0149	0.0287	4.63	4.59	0.0155	0.0079	0.0074
Butylbenzyl phthalate	0.109	0.0157	ND	0.032	0.857	0.445	1.69	2.17	0.551	0.235	0.0519
Dicyclohexyl phthalate	ND	0.1595	ND	0.0413	1.71	0.879	1.01	7	0.687	0.53	0.171
Alkylphenols											

Octylphenol	ND	ND	ND	0.048	6.49	3.27	2.91	1.78	0.0876	ND	ND
Nonylphenol	ND	ND	ND	0.0437	114	57.3	3.422	4.378	1.604	0.0974	0.0205

Table 4: Concentration of PAHs, PCBs, PEs and APs (in μg L^{-1}) in real environmental water samples. ND=Not Detected (below detection limit).

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Conclusions

In this work, a reliable method based on the use of HS-SPME and GC-MS/MS has been developed and validated for the simultaneous determination of 34 semi-volatile xenobiotics belonging to 4 compound families in environmental water samples. The analytical performance characteristics were calculated and high sensitivity and accuracy were achieved.

Five parameters affecting extraction recoveries were investigated and the optimal operating conditions obtained were 100 μm PDMS fiber, 15 ml of sample salted at 20% of NaCl and extraction at 80°C for 40 min. The SPME method exhibited good linearity on a wide range of concentration and yielded good recoveries and reproducibility, with sub μg L^{-1} range.

The headspace solid-phase microextraction procedure developed is simple, fast, environmental friendly as it does not need organic solvents. The proposed method is 2 to 10 folder sensitive than other reported methodologies.

Finally, the method was successfully applied to the analysis of rain, sea and ground waters showing the occurrence of some of the target PAHs, PCBs, PEs and APs. The methodology showed that is an effective tool to conduce environmental monitoring of four different families of compounds in a single analytical run and with low sample handling. The low amount of sample required is an advantage because carrying big amounts of samples from field is not necessary.

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