Journal of Chromatography A, 1214 (2008) 1–10

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Simultaneous preconcentration of a wide variety of organic pollutants in water samples
Comparison of stir bar sorptive extraction and membrane-assisted solvent extraction

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ARTICLE INFO

Article history:
Received 28 July 2008
Received in revised form 10 October 2008
Accepted 15 October 2008
Available online 19 October 2008

Keywords:
Stir bar sorptive extraction
Membrane-assisted solvent extraction
Large volume injection-programmed temperature vaporisation
Polycylic aromatic hydrocarbons
Polychlorinated biphenyls
Phthalate esters
Nonylphenols
Polybrominated biphenyls
Polybrominated diphenyl ethers
Water samples

ABSTRACT

Stir bar soptive extraction (SBSE) coupled to thermal desorption-gas chromatography–mass spectrometry (TD-GC–MS) and membrane-assisted solvent extraction (MASE) coupled to large volume injection-programmed temperature vaporisation-GC–MS (LVI-PTV-GC–MS) were optimised for the simultaneous determination of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalate esters (PEs), nonylphenols (NPs), polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) in water samples. In the case of SBSE-TD, variables affecting the extraction (extraction time, addition of sodium chloride or methanol and sample volume) and desorption (cryofocusing temperature, desorption time and temperature, vent pressure and desorption flow) were fitted for the simultaneous determination. The extraction solvent nature (*n*-hexane, cyclohexane, *n*-heptane, ethyl acetate, toluene, dichloromethane or cyclohexane:ethyl acetate mixtures), as well as the addition of methanol (0–30%) and sodium chloride (0–20%), the extraction temperature (30–60 °C), shaking speed (250–750 rpm) and extraction time (5–150 min) were studied for the simultaneous membrane-assisted preconcentration. Finally, PTV-LVI variables such as injection volume (100–600 μL), injection speed (10–40 $\mu L\,s^{-1}$), vent pressure (0–12.7 psi), vent time (0.05–0.8 min), vent flow (30–80 $mL\,min^{-1}$), cryofocusing temperature (20–70 °C), split flow (20–100 $mL\,min^{-1}$) and split time (1–5 min) were optimised. The optimisation was carried out by means of experimental design approaches in most of the cases. Precision (~3–19% for both SBSE-TD and MASE-LVI-PTV), accuracy (~80–120% for both SBSE-TD and MASE-LVI-PTV), limits of detection (LoDs) (0.1–222 $ng\,L^{-1}$ for MASE-LVI-PTV and 0.03–20.4 $ng\,L^{-1}$ for SBSE-TD in dependence of substance) and linearity (from 25 $ng\,L^{-1}$ up to at least 500 $ng\,L^{-1}$ for both procedures) were established for both procedures. Finally, the developed methods were applied to the determination of the free concentrations of PAHs, PCBs, PEs, NPs, PBBs and PBDEs in natural water samples (estuarine water and sea water) from the Bilbao estuary (Northern Spain) and comparable results were obtained with both procedures.

1. Introduction

One of the main problems for the analysis of organic pollutants in water samples is the low concentrations at which those analytes are present. On the basis of their occurrence and toxic properties, a large number of these compounds have been identified as priority hazardous substances by the European Union (EU), the US Environmental Protection Agency (EPA) and by several international organizations [1–3]. For these reasons, the simultaneous analysis of multiple organic pollutants is a helpful tool to get a clearer screening of the levels of different compounds in environmental samples.

Conventional preconcentration methods such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are being gradually replaced by other preconcentration procedures as a means to minimise the use of organic solvents (green chemistry) and allow the automatization of the analysis in order to improve the robustness of the analytical methods [4–6].

Stir bar sorptive extraction (SBSE) was first introduced by Baltussen et al. [7] and uses 50–300 μL of polydimethylsiloxane (PDMS) to preconcentrate different analytes from a variety of matrices [8]. SBSE does not employ organic solvents for the extraction of the analytes and, in that sense, it can be considered as an

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doi:10.1016/j.chroma.2008.10.060

environmental friendly extraction procedure. Besides, when SBSE is coupled to a thermal desorption unit (TDU) of a gas chromatograph, it can be considered as an on-line combination of an automatic preconcentration device. A recent review on SBSE theory and applications was written by David and Sandra [9].

Another recent alternative for miniaturised preconcentration of analytes is based on the use of membranes that protect the acceptor phase (extraction solvent) where the analytes from the donor phase (sample) are concentrated. Jönsson and Mathiasson introduced the use of porous membranes with this aim [10,11] and such membranes have been successfully applied to the extraction of both polar [12–14] and non-polar [15–17] compounds using different approaches. Another alternative is the use of non-porous membranes which were first described by Hauser and Popp [18] as membrane-assisted solvent extraction (MASE) for the determination of organochlorine compounds in water samples. When non-porous membranes are used, the analytes dissolve in the membrane material (i.e. polypropylene) and pass through it from the donor phase into the acceptor phase. The use of non-porous membranes allows the handling of very complex matrices and is preferred to exclude traces of water from the organic extract because water can adversely affect the gas chromatographic system. MASE uses low volumes of organic solvent (400–1000 μL) and combined with large volume injection (LVI) provides good limits of detection (LoDs). It has already been successfully applied to the extraction of a variety of organic pollutants [19–23].

The main aim of the present work is the optimisation and comparison of SBSE coupled to TD-GC–MS and MASE followed by LVI-PTV-GC–MS for the simultaneous analysis of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), phthalate esters (PEs) and nonylphenols (NPs) in water samples. Based on these two methods, the determination of those micro-organic contaminants will be feasible in water samples as required in many monitoring programmes [3].

2. Experimental

2.1. Reagents and chemicals

EPA PEs mix (2000 mg L^{-1} each in *n*-hexane), SS TCL PAH Mix (2000 mg L^{-1} each in benzene:methylene chloride 50:50), CEN PCB Congener Mix 1 (10 mg L^{-1} each in *n*-heptane) and Semivolatile Internal Standard Mix ([$^2H_8$]naphthalene, [$^2H_{10}$]phenanthrene, [$^2H_{10}$]biphenyl, [$^2H_{12}$]benzo[*a*]antracene, [$^2H_{12}$]benzo[*a*]pyrene, [$^2H_{12}$]benzo[*ghi*]perylene, 2000 mg L^{-1} each in methylene chloride) were supplied by Supelco (Walton-on-Thames, UK). The isotopically labelled standards [$^2H_4$]dimethyl phthalate, [$^2H_4$]diethyl phthalate, [$^2H_4$]dibutyl phthalate were supplied by Sigma–Aldrich (Seelze, Germany) and [$^2H_4$]di(2-ethylhexyl) phthalate was supplied by Tracer Tecnologías Analíticas (Madrid, Spain), all with a purity above 98%. The mixture of nonylphenols (Pestanal) was obtained from Riedel-de Haën (Seelze, Germany) and Igepal (nonylphenol mono- and diethoxylates) from Aldrich (Milwaukee, WI, USA) and [$^2H_4$]4-nonylphenol (99%) from Isotec-Sigma–Aldrich (Miamisburg, OH, USA). The standard solutions [[$^{13}C_{12}$]2,4,4′-trichlorobiphenyl, [$^{13}C_{12}$]2,3,3′,5,5′-pentachlorobiphenyl, [$^{13}C_{12}$]2,2′,3,3′,5,5′,6-heptachlorobiphenyl, 1 mg L^{-1} each in nonane] were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Bromodiphenyl Ethers Lake Michigan Study (BDE-LMS) Mix (10 mg L^{-1} each in isooctane), 2,4′,5-tribromobiphenyl B-031N (10 mg, 100% purity) and 2,2′,4,4′,5,5′-hexabromobiphenyl (10 mg and 98.9% purity) were supplied from Isostandards Material (Alalpardo, Madrid, Spain). 2,4-Dibromobiphenyl (25 mg, 99.2% purity) and 2,2′,4,5′,6-pentabromobiphenyl (10 mg L^{-1} in cyclohexane) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The standard solutions [[$^{13}C_{12}$]3,3′,4,4′-tetrabromodiphenyl ether, [$^{13}C_{12}$]3,3′,4,4′,5-pentabromodiphenyl ether, 100 and 150 μg L^{-1}, respectively, in *n*-nonane] were obtained from Cambridge Isotope Laboratories.

The solvents *n*-hexane, cyclohexane, *n*-heptane, ethyl acetate, toluene, acetone and dichloromethane (HPLC grade) were purchased from Labscan (Labscan, Dublin, Ireland).

All the gases used in the detection step (He and N_2) were supplied by Carburos Metálicos (99.9995%, Barcelona, Spain).

2.2. Preparation of standards

All the solutions were diluted in HPLC-grade acetone (Labscan) and a working solution containing all the compounds studied was prepared at a concentration of 50 μg L^{-1}. Samples were daily prepared in Milli-Q water (<0.05 μS cm^{-1}) after spiking with the corresponding working solutions in concentrations between 25 and 500 ng L^{-1} for all the analytes investigated.

Sodium chloride (Merck, Darmstadt, Germany) and HPLC-grade methanol (HPLC grade, Labscan) were used for matrix modification experiments. NaCl was ultrasonically cleaned with methylene chloride (HPLC grade, LabScan) and dried at 150 °C before use.

Estuarine water and seawater were sampled at middle tide from the Bilbao estuary (Northern Spain) in three different sampling points (Udondo, Lamiako and Getxo) in May 2008. Samples were collected in 500 mL bottles, which contained 100 mL of methanol, and carried to the laboratory in cooled boxes. Once in the laboratory, samples were filtered through 0.45 μm filters (47 mm diameter cellulose nitrate membrane filters, Whatman, Maidstone, UK) and analysed within 24 h.

2.3. SBSE-TD-GC–MS

The stir bars employed (so-called Twisters supplied by Gerstel, Mülheim an der Ruhr, Germany) were 10 mm length and 0.5 mm film thick. Prior to use, the stir bars were conditioned in an empty thermal desorption tube at 300 °C for 4 h with helium at a flow desorption rate of 50 mL min^{-1}. Stirring was carried out using a 15 position magnetic stirrer (Gerstel).

Under optimal conditions the stir bars were introduced in 20 mL aliquots of the water samples (spiked or natural) which contained 20% (m/v) of NaCl and 20% (v/v) of methanol according to two previous works of our research group [24,25]. Once the extraction step (12 h) was over, the stir bars were rinsed with Milli-Q water in order to eliminate the NaCl and dried carefully with a paper tissue before introduction into a glass desorption tube. The stir bars were thermally desorbed for 10 min at 300 °C using a commercial thermal desorption TDS-2 unit (Gerstel) connected to a CIS-4 injector (Gerstel). The desorption unit was installed in an Agilent 6890 gas chromatograph coupled to an Agilent 5975 mass spectrometer system (Agilent Technologies, Palo Alto, CA, USA). The TDS-2 was equipped with a TDSA auto sampler (Gerstel) able to handle 98 coated stir bars. All glass tubes containing the stir bars were placed in a tray which was assembled in the TDSA auto sampler. The desorption flow and vent pressure were fixed at 23 mL min^{-1} and 7 psi, respectively, according to previous works [24,25], while the temperature of the CIS-4 for the simultaneous determination was fixed at −10 °C.

Analytes were separated on a HP-5MS (30 m × 0.25 mm, 0.25 μm, Agilent) column. The oven temperature was programmed as follows: start at 50 °C for 2 min, increase at 15 °C min^{-1} to 100 °C, increase at 10 °C min^{-1} to 290 °C and held at 290 °C for 15 min to achieve a running time of 39.33 min. The transfer line, ion source

Table 1
The ions monitored for each analyte studied and the corresponding internal standards. The first ion was used as quantifier and the second one as qualifier.

Compound	*m/z*	Internal standard	*m/z*
Polycyclic aromatic hydrocarbons (PAHs)			
Naphthalene (Nap)	128, 129	[$^2H_8$]Naphthalene ([$^2H_8$]Nap)	136, 137
Acenaphthylene (Acy)	152, 153	[$^2H_{10}$]Biphenyl ([$^2H_{10}$]Byp)	164, 163
Acenaphthene (Ace)	153, 154	[$^2H_{10}$]Biphenyl ([$^2H_{10}$]Byp)	164, 163
Fluorene (Flu)	165, 166	[$^2H_{10}$]Biphenyl ([$^2H_{10}$]Byp)	164, 163
Phenanthrene (Phe)	178, 179	[$^2H_{10}$]Phenanthrene ([$^2H_{10}$]Phe)	188, 190
Anthracene (Ant)	178, 179	[$^2H_{10}$]Phenanthrene ([$^2H_{10}$]Phe)	188, 190
Fluoranthene (Flr)	202, 203	[$^2H_{10}$]Phenanthrene ([$^2H_{10}$]Phe)	188, 190
Pyrene (Pyr)	202, 203	[$^2H_{10}$]Phenanthrene ([$^2H_{10}$]Phe)	188, 190
Benzo[*a*]anthracene (B[*a*]A)	228, 229	[$^2H_{12}$]Benzo[*a*]anthracene ([$^2H_{12}$]B[*a*]A)	240, 126
Chrysene (Chr)	228, 229	[$^2H_{12}$]Benzo[*a*]anthracene ([$^2H_{12}$]B[*a*]A)	240, 126
Benzo[*b*]fluoranthene (B[*b*]F)	252, 253	[$^2H_{12}$]Benzo[*a*]pyrene ([$^2H_{12}$]B[*a*]P)	264, 138
Benzo[*k*]fluoranthene (B[*k*]F)	252, 253	[$^2H_{12}$]Benzo[*a*]pyrene ([$^2H_{12}$]B[*a*]P)	264, 138
Benzo[*a*]pyrene (B[*a*]P)	252, 253	[$^2H_{12}$]Benzo[*a*]pyrene ([$^2H_{12}$]B[*a*]P)	264, 138
Dibenzo[*a,h*]anthracene (D[*ah*]A)	276, 277	[$^2H_{12}$]Benzo[*ghi*]perylene ([$^2H_{12}$]B[*ghi*]P)	288, 150
Benzo[*ghi*]perylene (B[*ghi*]P)	276, 277	[$^2H_{12}$]Benzo[*ghi*]perylene ([$^2H_{12}$]B[*ghi*]P)	288, 150
Indene[1,2,3-*cd*]pyrene (Ind)	276, 277	[$^2H_{12}$]Benzo[*ghi*]perylene ([$^2H_{12}$]B[*ghi*]P)	288, 150
Nonylphenols and nonylphenols ethoxylates			
Nonylphenol (NP)	149, 135	[$^2H_4$]4-Nonylphenol ([$^2H_4$]4-NP)	111, 224
Nonylphenol monoethoxylate (NP1EO)	193, 179	[$^2H_4$]4-Nonylphenol ([$^2H_4$]4-NP)	111, 224
Nonylphenol diethoxylate (NP2EO)	223, 237	[$^2H_4$]4-Nonylphenol ([$^2H_4$]4-NP)	111, 224
Polychlorinated biphenyls (PCBs)			
2,2′,5-Trichlorobiphenyl (CB-18)	186, 256	[$^{13}C_{12}$]2,4,4′-Trichlorobiphenyl ([$^{13}C_{12}$]CB-28)	270, 198
2,4,4′-Trichlorobiphenyl (CB-28)	256, 186	[$^{13}C_{12}$]2,4,4′-Trichlorobiphenyl ([$^{13}C_{12}$]CB-28)	270, 198
2,4′,5-Trichlorobiphenyl (CB-31)	256, 186	[$^{13}C_{12}$]2,4,4′-Trichlorobiphenyl ([$^{13}C_{12}$]CB-28)	270, 198
2,2ĭ,5,5′-Tetrachlorobiphenyl (CB-52)	292, 220	[$^{13}C_{12}$]2,4,4′-Trichlorobiphenyl ([$^{13}C_{12}$]CB-28)	270, 198
2,2ĭ,3,5′-Tetrachlorobiphenyl (CB-44)	292, 220	[$^{13}C_{12}$]2,4,4′-Trichlorobiphenyl ([$^{13}C_{12}$]CB-28)	270, 198
2,2ĭ,4,5,5′-Pentachlorobiphenyl (CB-101)	326, 256	[$^{13}C_{12}$]2,3,3′,5,5′-Pentachlorobiphenyl ([$^{13}C_{12}$]CB-111)	338, 268
2,3ĭ,4,4ĭ,5-Pentachlorobiphenyl (CB-118)	326, 256	[$^{13}C_{12}$]2,3,3′,5,5′-Pentachlorobiphenyl ([$^{13}C_{12}$]CB-111)	338, 268
2,2′,4,4′,5,5′-Hexachlorobiphenyl (CB-153)	360, 290	[$^{13}C_{12}$]2,3,3′,5,5′-Pentachlorobiphenyl ([$^{13}C_{12}$]CB-111)	338, 268
2,2′,3,4,4′,5′-Hexachlorobiphenyl (CB-138)	360, 290	[$^{13}C_{12}$]2,3,3′,5,5′-Pentachlorobiphenyl ([$^{13}C_{12}$]CB-111)	338, 268
2,2ĭ,3,4′,5′,6-Hexachlorobiphenyl (CB-149)	360, 290	[$^{13}C_{12}$]2,3,3′,5,5′-Pentachlorobiphenyl ([$^{13}C_{12}$]CB-111)	338, 268
2,2′,3,4,4′,5,5′-Heptachlorobiphenyl (CB-180)	394, 324	[$^{13}C_{12}$]2,2′,3,3′,5,5′,6-Heptachlorobiphenyl ([$^{13}C_{12}$]CB-178)	409, 371
2,2′,3,3′,4,4′,5,5′-Octachlorobiphenyl (CB-194)	430, 360	[$^{13}C_{12}$]2,2′,3,3′,5,5′,6-Heptachlorobiphenyl ([$^{13}C_{12}$]CB-178)	409, 371
Phthalate esters (PEs)			
Dimethyl phthalate (DMP)	77, 163	[$^2H_4$]Dimethyl phthalate ([$^2H_4$]DMP)	167
Diethyl phthalate (DEP)	149, 177	[$^2H_4$]]Diethyl phthalate [$^2H_4$](DEP)	153, 181
Di-*n*-butyl phthalate (DBP)	104, 149	[$^2H_4$]Di-*n*-butyl phthalate ([$^2H_4$]DBP)	153
n-Butyl benzyl phthalate (BBP)	91, 149	[$^2H_4$]Di-*n*-butyl phthalate ([$^2H_4$]DBP)	153
Di(2-ethylhexyl) phthalate (DEHP)	149, 167	[$^2H_4$]Bis(2-ethylhexyl) phthalate ([$^2H_4$]DEHP)	153, 171
Di-*n*-octyl phthalate (DOP)	149, 279	[$^2H_4$]Bis(2-ethylhexyl) phthalate ([$^2H_4$]DEHP)	153, 171
Polybrominated diphenyl ethers (PBDEs)			
2,4,4′-Tribromodiphenyl ether (BDE-28)	406, 408	[$^{13}C_{12}$]3,3′,4,4′-tetrabromodiphenyl ether ([$^{13}C_{12}$]]BDE-77)	496, 498
2,2′,4,4′-Tetrabromodiphenyl ether (BDE-47)	486, 484	[$^{13}C_{12}$]3,3′,4,4′-tetrabromodiphenyl ether ([$^{13}C_{12}$]]BDE-77)	496, 498
2,3′,4,4′-Tetrabromodiphenyl ether (BDE-66)	486, 484	[$^{13}C_{12}$]3,3′,4,4′-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-77)	496, 498
2,2′,3,4,4′-Pentabromodiphenyl ether (BDE-99)	404, 564	[$^{13}C_{12}$]3,3′,4,4′,5-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-126)	418, 404
2,2′,4,4′,5-Pentabromodiphenyl ether (BDE-100)	404, 564	[$^{13}C_{12}$]3,3′,4,4′,5-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-126)	418, 404
2,2′,4,4′,6-Pentabromodiphenyl ether (BDE-85)	404, 564	[$^{13}C_{12}$]3,3′,4,4′,5-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-126)	418, 404
2,2′,3,4,4′,5′-Hexabromodiphenyl ether (BDE-138)	484, 644	[$^{13}C_{12}$]3,3′,4,4′,5-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-126)	418, 404
2,2′,4,4′,5,5′-Hexabromodiphenyl ether (BDE-153)	484, 644	[$^{13}C_{12}$]3,3′,4,4′,5-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-126)	418, 404
2,2′,4,4′,5,6′-Hexabromodiphenyl ether (BDE-154)	484, 644	[$^{13}C_{12}$]3,3′,4,4′,5-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-126)	418, 404
Polybrominated biphenyls (PBBs)			
2,4-Dibromobiphenyl (BB-7)	312, 152	[$^{13}C_{12}$]3,3′,4,4′-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-77)	496, 498
2,4′,5-Tribromobiphenyl (BB-31)	390, 232	[$^{13}C_{12}$]3,3′,4,4′-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-77)	496, 498
2,2′,4,5′,6-Pentabromobiphenyl (BB-103)	469, 548	[$^{13}C_{12}$]3,3′,4,4′,5-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-126)	418, 404
2,2′,4,4′,5,5′-Hexabromobiphenyl (BB-153)	628, 468	[$^{13}C_{12}$]3,3′,4,4′,5-tetrabromodiphenyl ether ([$^{13}C_{12}$]BDE-126)	418, 404

and quadrupole analyser temperatures were maintained at 300, 230 and 150 °C, respectively, and a solvent delay of 8 min was selected. Detection was carried out using electron impact ionisation at selected ion monitoring (SIM) mode. The ions monitored for each analyte are summarised in Table 1. The first ion was used as quantifier and the second one as qualifier.

2.4. MASE-LVI-PTV-GC–MS

The device used for membrane-assisted solvent extraction was manufactured by Gerstel (Mülheim, Germany). The extraction cell consists of a conventional 20 mL headspace-vial which is filled with 15 mL of aqueous sample. High-density polypropylene membrane bags (4 cm long with a wall thickness of 0.03 mm and an internal diameter of 6 mm) were attached to a metal funnel and fixed with Teflon rings. Vials were closed with metallic crimp caps enabling magnetic transport between sample tray and stirrer unit. Extraction vials were placed into the tray of the multipurpose sampler (MPS 2) and the membrane bags were automatically filled with an organic solvent (50:50 ethyl acetate:cyclohexane as optimal for the simultaneous extraction). Under optimal conditions water samples contained 20% (m/v) NaCl and 20% (v/v) methanol. The vials were transported to the stirrer and shaken at optimised temperature (50 °C), shaking speed (500 rpm) and time (60 min). Then, the

vial was magnetically removed from the stirrer by the sampler and transported to the sample tray. The organic extracts were transferred to 2 mL vials and from those automatically withdrawn and injected into the inlet of the gas chromatograph using a 1000 μL syringe.

Prior to use, the membrane bags were conditioned by shaking with *n*-hexane at room temperature for 1 h in an ultrasound bath and then kept overnight in clean *n*-hexane. This procedure ensures the removal of memory effects and decreases the amount of interfering compounds from the membrane material [26].

LVI was carried out using the MPS 2 with a 1000 μL syringe. The injection system consisted of a septumless head and a temperature programmable injector (cooled injection system CIS-4, Gerstel) equipped with an empty baffled deactivated glass liner. During LVI-PTV injection and under optimum conditions, the inlet temperature was held at 70 °C by cooling with a liquid nitrogen, while the column head pressure was fixed to 12.7 psi and the flow rate through the split vent was set at 70 mL min^{-1} in order to purge out most of the solvent. At a vent time of 0.7 min the split valve was closed for 1.5 min. The temperature program of the injector was chosen as follows: 70 °C for 0.5 min, 12 °C s^{-1} to 250 °C for 1 min and finally 12 °C s^{-1} to 330 °C for 3 min (cleaning step). The optimised injection volume was set at 300 μL.

Detection was carried out using the SIM mode (see Table 1 for the *m*/*z* values followed) under the same GC–MS conditions mentioned before for TD-GC–MS.

3. Results and discussion

3.1. Optimisation of the simultaneous SBSE-TD-GC–MS

In order to fix the conditions for the simultaneous SBSE preconcentration followed by TD-GC–MS analysis of PAHs, PCBs, PEs, NPs, PBDEs and PBBs, the results obtained in two previous works of our research group were considered [23]. Those two works studied the simultaneous SBSE preconcentration of PAHs, PCBs, PEs and NPs [24] on the one hand and the simultaneous preconcentration of PBDEs and PBBs [25] on the other.

Four parameters affecting the extraction conditions were studied in those two previous works: (i) the addition of NaCl (0–20%, m/v), (ii) the addition of methanol (0–30%, v/v), (iii) the sample volume (5–100 mL) and (iv) extraction time (5–1800 min). 20 mL of sample which contained 20% (m/v) of NaCl and 20% (v/v) of methanol were extracted with a 10 mm length × 0.5 mm thickness PDMS stir bar for 12 h as consensus conditions.

In the case of the desorption conditions the influence of (i) desorption time, (ii) desorption temperature, (iii) desorption flow, (iv) cryofocusing temperature and (v) vent pressure was studied in the previously mentioned works. Consensus desorption conditions based on the previous works were settled down for the following variables: desorption temperature (300 °C), desorption time (10 min), desorption flow (23 mL min^{-1}) and vent pressure (7 psi). In the case of the CIS-4 temperature, in a first approach it was decided to fix it at −50 °C but it was observed that PBDEs, PBBs, some PEs and NPEOs were discriminated under those conditions. Since the common cryofocusing temperature seemed to influence in the greatest extent the sensitivity of the analytes studied, it was decided to study a range of temperatures (−40 to 20 °C) before choosing the most suitable value. Experiments were carried out using spiked samples at 500 ng L^{-1} which were desorbed at four different cryofocusing temperatures (−40, −20, 0 and 20 °C). The average values of three replicates are shown in Fig. 1. In order to visualize more easily the results, the responses are shown as the normalised average chromatographic peak areas.

As it can be observed from the results in Fig. 1, a wide variety of analytes (Phe, CB-118, CB-180, BB-31, BDE-47, NP, NP1EO and NP2EO) were best determined when the cryofocusing temperature was set at 0 °C. In the case of B[*a*]A [27], B[*a*]P, BB-7, BDE-28, BDE-100 and BBP room temperature seemed to be optimum (20 °C). It should be underlined that most of those analytes are some of the least volatile of each family. However, in the case of Nap, CB-28 and DOP best responses were obtained at temperatures below 0 °C. Even if according to the results shown 0 °C could seem to be the adequate compromise cryofocusing temperature, it was decided to fix it at −10 °C because the response of Nap was greatly affected at higher temperature values.

3.2. Optimisation of the simultaneous MASE

The first variable studied for the simultaneous MASE preconcentration of PAHs, PCBs, PEs, NPs, NPEOs, PBBs and PBDEs was the extraction solvent (acceptor phase). Several factors were considered in order to choose the solvents that should be investigated. Firstly, the boiling point of the solvent should be higher than 30 °C since this is the lowest temperature that can be achieved in the stirring system used for the incubation of the samples. On the other hand, since a large volume (≥100 μL) of the extract had to be injected in the PTV injector, the solvents studied should be volatile enough to be removed through the split outlet. Finally, the polarity of the analytes ranged from the most non-polar PBBs or PCBs to the

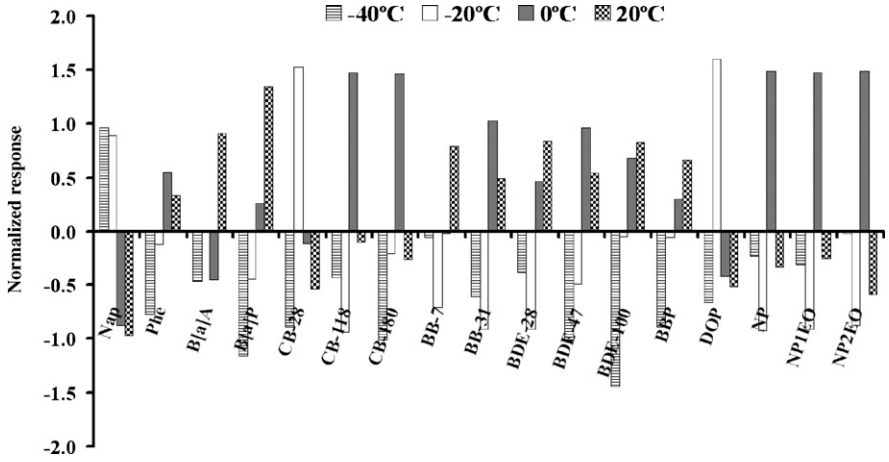

Fig. 1. Average normalised chromatographic peak areas obtained in the study of the compromise cryofocusing temperature for the SBSE-TD-GC–MS analysis.

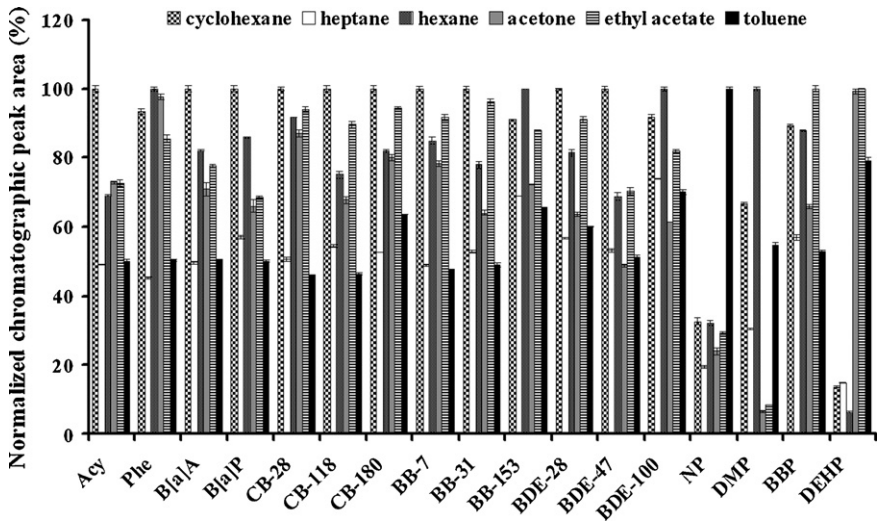

Fig. 2. Comparison of the normalised average responses ($n = 3$) obtained for the different solvents used as acceptors in MASE preconcentration of several of the analytes studied.

more polar NPs. In this sense the polarity of the solvents also ranged from more polar solvents such as ethyl acetate that have yielded good results for phenols [8], to more non-polar solvents such as cyclohexane which have proved optimal results for analytes such as PCBs [28].

Thus, seven different solvents (*n*-hexane, cyclohexane, *n*-heptane, ethyl acetate, toluene, acetone and dichloromethane) were studied for the simultaneous preconcentration and the results (as the normalised average chromatographic peak area of three replicates) are shown in Fig. 2. Dichlorometane, *n*-heptane and toluene showed poor enrichment factors for the majority of the target analytes, except in the case of toluene for DEHP and NP. Ethyl acetate, cyclohexane and *n*-hexane demonstrated good yields for the majority of analytes as shown in Fig. 2. Therefore, the use of ethyl acetate and cyclohexane mixtures were further considered during the optimisation of the rest of variables that can affect the preconcentration step.

Different variables affecting the MASE preconcentration were studied: (i) the addition of methanol (0–30%, v/v), which avoids the adsorption of non-polar compounds [27,29,30], (ii) the addition of NaCl (0–20%, m/v), which modifies the solvatation ability of water (salting out/in effect), (iii) the extraction temperature (30–60 °C), (iv) the solvent nature (20:80 to 80:20% cyclohexane–ethyl acetate mixture) and (v) the stirring speed (250–750 rpm). In a first approach a two-level fractional factorial design with the central point in triplicate was built by means of the Unscrambler program (Camo, Norway). In this case the shaking speed variable was defined as a combination of the rest of variables in order to reduce the number of the experiments ($2^{5-1} + 3$).

Table 2 summarises the significant *B* coefficients (p-value < 0.05) and the correlation coefficients (r) obtained after multiple linear regression (MLR) for some selected compounds under study (Nap, Phe, B[*a*]A, B[*a*]P, CB-28, CB-118, CB-180, BB-7, BB-31, BB-153, BDE-28, BDE-47, BDE-100, BDE-154, DMP, BBP, DEHP, NP, NP1EO + NP2EO) from the data obtained in the fractional factorial design. p-Values lower than 0.05 mean that the probability of the parameter to be 0 is lower than a 5%. In the case of Phe ($r = 0.95$), B[*a*]A ($r = 0.94$), CB-118 ($r = 0.92$), CB-180 ($r = 0.95$), BB-7 ($r = 0.92$), BB-31 ($r = 0.91$), BDE-28 ($r = 0.93$), BDE-47 ($r = 0.96$), NP ($r = 0.91$), NP1EO + NP2EO ($r = 0.93$), BBP ($r = 0.93$) and DEHP ($r = 0.91$) insignificant B coefficients were obtained in all the cases (p-value > 0.05). Based on the overall results, we decided to fix the amount of methanol and NaCl at 20% and the shaking rate at 500 rpm before extending this factorial design to a central composite design (CCD).

This way in the CCD only the extraction temperature and the solvent composition were studied in depth. The significant B coef-

Table 2
Significant regression parameters (B) (p-value < 0.05) and correlation coefficients (r) obtained in the fractional factorial design for the optimisation of the MASE preconcentration step: A ≡ methanol addition; B ≡ NaCl addition; C ≡ extraction temperature; D ≡ cyclohexane percentage; E ≡ shaking speed.

Congener	Nap	B[*a*]P	CB-28	BB-153	BDE-100	BDE-154	DMP
B_A	5.4×10^3	1.4×10^5	5.2×10^4	2.5×10^3	7.4×10^3	4.0×10^3	-1.6×10^4
B_B	5.4×10^3	1.8×10^5	–[a]	5.0×10^3	1.1×10^4	6.8×10^3	3.3×10^4
B_C	2.8×10^3	9.3×10^4	–	3.2×10^3	7.1×10^3	4.7×10^3	–
B_D	2.6×10^3	5.4×10^4	–	0.6×10^3	–	1.1×10^3	–
B_E	-2.1×10^2	–	–	–	–	–	–
B_{AB}	–	–	–	1.4×10^4	–	5.1×10^4	–
B_{AC}	–	–	–	3.7×10^4	7.6×10^4	3.8×10^4	–
B_{AD}	–	–	–	2.0×10^4	–	-4.1×10^4	–
B_{AE}	-5.4×10^4	-1.6×10^6	-6.4×10^5	-3.4×10^4	-8.2×10^4	–	–
B_{BC}	4.2×10^4	1.9×10^6	–	1.4×10^4	1.1×10^5	–	–
B_{BD}	–	–	–	–	–	–	–
B_{BE}	–	1.4×10^6	–	2.2×10^4	–	2.9×10^4	–
B_{CD}	–	-1.4×10^6	–	–	–	–	–
B_{DE}	–	2.7×10^6	9.3×10^5	3.7×10^4	–	3.9×10^4	–
r	0.99	0.99	0.99	0.99	0.99	0.99	0.98

[a] p-value > 0.05.

Table 3
Significant regression parameters (B) (p-value < 0.05) and correlation coefficients (r) obtained in the CCD for the optimisation of the MASE preconcentration: A ≡ temperature; B ≡ cyclohexane percentage in the cycloehexane:ethyl acetate mixture.

Congener	B_A	B_B	B_{AB}	B_{AA}	B_{BB}	r
Nap	–[a]	–	–	–	–	0.75
Phe	–	–	–	–	–	0.82
B[a]A	1.3×10^5	-6.4×10^4	–	–	–	0.92
B[a]P	9.7×10^4	–	–	–	–	0.91
CB-28	–	–	–	–	–	0.90
CB-118	–	–	–	–	–	0.82
CB-180	1.9×10^4	–	–	–	–	0.85
BB-7	4.4×10^4	–	–	–	–	0.84
BB-31	3.7×10^4	–	–	–	4.4×10^5	0.93
BB-153	3.7×10^3	–	–	–	–	0.84
BDE-28	1.4×10^4	–	–	–	–	0.85
BDE-47	1.2×10^4	–	–	–	–	0.88
BDE-100	7.2×10^3	–	–	–	–	0.86
BDE-154	–	–	–	-9.3×10^4	–	0.92
DMP	–	–	–	–	–	0.80
BBP	2.1×10^5	–	–	–	1.0×10^6	0.93
DEHP	–	–	–	-3.2×10^6	-2.1×10^6	0.92
NP	9.9×10^4	–	–	–	–	0.87
NP1EO + NP2EO	6.2×10^4	–	–	–	–	0.91

[a] p-value > 0.05.

Table 4
Analysis of effects obtained for the Plackett–Burman design used in the optimisation of the LVI-PTV injection step (Significance Testing Method: Center).

Variables	Phe	B[a]A	B[a]P	CB-28	CB-118	CB-180	BB-7	BB-153	BDE-47	BDE-100	BDE-154	NP	NP1EO + NP2EO	BBP	DEHP
Vent pressure (A)	+	NS	+	NS	NS	NS	+	NS	NS	NS	NS	NS	NS	NS	+
Cryofocusing temperature (B)	++	NS	NS	+	++	NS	++	+	NS	+	+	NS	+	+	++
Vent time (C)	–	–	– –	NS	– –	–	–	– –	–	– –	– –	–	– –	–	++
Vent flow (D)	+	+	+	NS	++	NS	+	+	+	+	+	NS	– –	+	++
Split flow (E)	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	+	– –	NS	+
Split time (F)	NS	+	+	NS	+	NS	NS	+	+	+	+	+	++	+	+++
Injection volumen (G)	NS	NS	NS	NS	NS	NS	+	NS	NS	NS	NS	NS	– –	NS	+++
Injection speed (H)	NS	NS	+	NS	+	NS	NS	+	NS	+	+	–	+	NS	NS

NS ≡ no significant; '+' ≡ positive effect; '++' ≡ high-positive effect; '+++' ≡ very high-positive effect; '–' ≡ negative effect; '– –' ≡ high-negative effect.

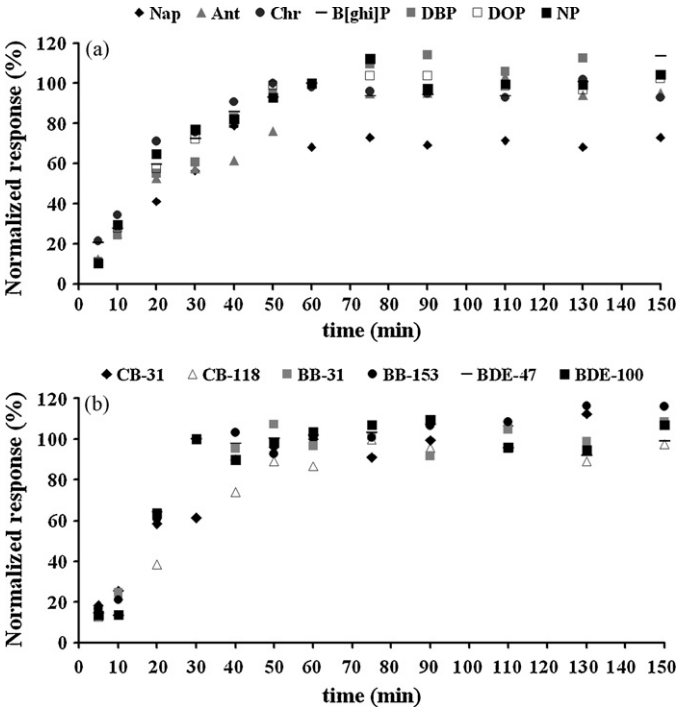

Fig. 3. Extraction time profiles for MASE of some selected analytes: (a) PAHs, PEs and NPs; (b) PCBs, PBBs and PBDEs.

ficients (p-value < 0.05) and correlation coefficients (r) obtained after the multiple linear regressions (MLR) of some representative analytes are included in Table 3. In the case of the extraction temperature, the best responses were obtained for high temperatures (positive B_A parameter), except for BDE-154 and DEHP. These last two analytes showed a negative squared B_{AA} term. Thus, the extraction temperature was fixed at an intermediate-high value of 50 °C. On the other hand, the cyclohexane percentage was set at an intermediate value (50%) since it was no significant for the majority of the studied compounds.

In order to check at which time equilibrium was reached during MASE preconcentration, the extraction time profiles of the analytes studied were investigated by stirring spiked (100 ng L^{-1}) samples at different extraction periods (5–150 min) under the conditions optimised before. The results obtained for selected PAHs, PEs and NPs are shown in Fig. 3a and those for PCBs, PBBs and PBDEs in Fig. 3b. Equilibrium was attained after 50–60 min in the case of PAHs, PEs and NPs. In the case of PCBs, PBBs and PBDEs systematically shorter extraction periods were necessary in order to obtain the equilibrium (20–40 min). In order to assure that all the analytes were extracted under equilibrium, a 60 min extraction was chosen. The extraction time profiles obtained are similar to those obtained in other works for some PAHs [31], PCBs [18,26,32] and phenols [33].

3.3. Optimisation of the LVI-PTV injection

During LVI-PTV injection in gas chromatography there are many variables that could affect the injection since it must be assured

Table 5
Significant regression parameters (B) (p-value < 0.1) and correlation coefficients (r) obtained in the CCD for the optimisation of the injection step: A ≡ vent time; B ≡ vent flow; C ≡ split flow.

Congener	B_A	B_B	B_C	B_{AB}	B_{AC}	B_{BC}	B_{AA}	B_{BB}	B_{CC}	r
Nap	–[a]	-6.4×10^4	–	–	–	–	–	–	–	0.75
Phe	–	–	–	–	–	–	–	2.3×10^6	–	0.74
B[*a*]A	1.4×10^7	–	–	–	–	–	-2.210^6	–	–	0.92
B[*a*]P	5.2×10^6	–	–	–	–	–	-1.1×10^6	–	–	0.93
CB-28	–	–	–	-1.1×10^6	–	–	-1.3×10^6	–	–	0.90
CB-118	8.2×10^6	–	–	–	–	–	-7.9×10^5	–	–	0.95
CB-180	3.4×10^6	–	–	–	–	–	-4.3×10^5	–	–	0.92
BB-7	–	–	–	-7.2×10^5	–	–	-6.9×10^5	–	–	0.85
BB-31	5.9×10^6	–	–	-5.9×10^5	–	–	-5.3×10^5	–	5.1×10^5	0.95
BB-153	1.5×10^5	1.1×10^3	–	–	–	–	-1.9×10^4	–	–	0.98
BDE-28	2.2×10^6	–	–	–	–	–	-2.1×10^5	–	–	0.93
BDE-47	1.5×10^6	6.4×10^3	–	–	–	–	-1.8×10^5	–	–	0.94
BDE-100	5.5×10^5	–	–	–	–	–	–	–	–	0.90
BDE-154	8.3×10^4	5.1×10^2	–	–	–	–	-9.3×10^3	–	–	0.93
DMP	1.5×10^6	–	–	–	–	–	2.1×10^5	3.2×10^5	2.9×10^5	0.96
BBP	8.1×10^6	–	–	–	–	–	-1.2×10^6	–	–	0.90
DEHP	–	–	–	–	–	–	-3.7×10^6	–	–	0.80
NP	–	-2.7×10^3	–	–	–	–	–	6.2×10^4	–	0.85
NP1EO + NP2EO	5.5×10^5	–	–	–	–	–	–	–	–	0.92

[a] p-value > 0.1.

that the solvent is eliminated through the split vent while the analytes are trapped in the CIS-4 unit. In this sense, since the amount of variables is too high, the following variables were screened by means of a Plackett–Burman design built in the Unscrambler program: (i) vent pressure (0–12.7 psi), (ii) vent time (0.05–0.8 min), (iii) vent flow (30–80 mL min^{-1}), (iv) cryofocusing temperature (20–70 °C), (v) split flow (20–100 mL min^{-1}), (vi) split time (1–5 min), (vii) injection volume (100–600 μL) and (viii) injection speed (10–40 μL s^{-1}).

As responses, both the peak area and peak width (full width at half maximum) were measured and the ratio of them was calculated as a combined response.

According to the analysis of effects of the results obtained (see Table 4) vent pressure had either a positive effect (Phe, B[*a*]P, BB-7 and DEHP) or no significant effect (B[*a*]A, CB-28, CB-118, CB-180, BB-153, BDE-47, BDE-100, BDE-154, NP, NP1EO + NP2EO and BBP) and thus it was decided to fix it at the highest value studied (12.7 psi). A similar behaviour was observed for the cryofocusing temperature: it either had a positive effect (Phe, CB-28, CB-118, BB-7, BB-153, BDE-100, BDE-154, NP1EO + NP2EO, BBP and DEHP) or was not significant (B[*a*]A, B[*a*]P, CB-180, BDE-47 and NP) and, thus, it was decided to set it also at the highest value studied (70 °C). In the case of the split time, a positive effect of this variable was observed and, in a first approach, it was decided to fix it at a high value (~4 min). However, it was observed that when such long split times were used repeatedly, the chromatographic system was contaminated and, thus, we were forced to set it at 1.5 min. In the case of the injection volume, this variable was almost not significant for most of the analytes and, since repeated injections of high volumes can cause problems in the PTV injector, the injection volume was fixed at 300 μL. Finally, the injection speed had a positive effect for most of the analytes and, in this sense, a 30 μL s^{-1} speed was chosen.

The rest of the variables (i.e. vent time, vent flow and split flow) were further optimised by means of a CCD. The results of the MLR are included in Table 5. In the case of the split flow, it only affected (and positively) the response of BB-31 and DMP and since this parameter did not affect the rest of the analytes, it was decided to fix it at a high value (80 mL min^{-1}). In the case of vent time, this parameter affected the response of almost all the analytes and, although the squared term (B_{AA}) in most of the cases and the B_{AB} term in the case of CB-28, BB-7 and BB-31 are negative, the major influence of the positive linear term (B_A) in most cases clearly indicated that the best responses were obtained at a high-vent time value. Thus, 0.7 min vent time was chosen. Finally, the vent flow had a similar effect on the analytes studied. Intermediate flows were more suitable for most of the analytes and an intermediate value of 70 mL min^{-1} was chosen.

3.4. Validation of SBSE-TD-GC–MS and MASE-LVI-PTV-GC–MS determinations

In order to study the linearity of SBSE-TD-GC–MS and MASE-LVI-PTV-GC–MS, calibration curves were built in the 25–500 ng L^{-1} range. Good correlation coefficients ($r^2 \geq 0.99$) were obtained for all the analytes and with both preconcentration techniques after correction with the corresponding internal standards.

Before calculating the limits of detection (LoDs) and quantification (LoQs), a twofold extraction of the membranes at room temperature using a mixture of cyclohexane and ethyl acetate at 50:50 was performed using an ultrasound bath before the MASE procedure. In the case of the stir bars it was not necessary to condition the twisters after each analysis.

The LoDs and LoQs were calculated as the signal of the blank plus 3 or 10 times the standard deviation of four blank extractions, respectively. When no peaks were found at the retention time of the analyte, the LoDs and LoQs were estimated as 3 or 10 times the signal-to-noise (S/N) ratio, respectively. In the case of nonylphenols the same retention times integrated for the standards were considered in order to calculate the LoDs and LoQs. The results obtained are included in Table 6.

In the case of PAHs, PCBs, PBBs and PBDEs similar values were obtained by both MASE and SBSE. In the case of PEs and NPs, however, the values obtained for SBSE were significantly better. In the case of PEs this could be due to the use of phthalates in the manufacture of polymers such as the one used in the membrane. The LoDs obtained are lower than those obtained in other works for PAHs [31] and PCBs [26] in the case of MASE methodology. In the case of SBSE preconcentration the LoDs obtained are similar to those found in the bibliography for PAHs [34–36], PCBs [34,35], PBDEs [30] and PEs [37] following different methodologies. The LoDs and LoQs obtained in our previous works for SBSE [24,25] are similar to those obtained in the present work (see Table 6), although in the case of NPs and NPEOs the LoDs obtained previously are better than those obtained in this study, probably due to the discrimination under the compromise values chosen in the present work.

Table 6
Recoveries (%), LoDs (ng L^{-1}) ands LoQs (ng L^{-1}) obtained for the analytes studied in Milli-Q water (SIM mode) after extraction by MASE-LVI-PTV-GC–MS and SBSE-TD-GC–MS.

Compound	MASE-LVI-PTV-GC–MS (SIM) (this work)			SBSE-TD-GC–MS (SIM) (this work)			SBSE-TD-GC–MS (SIM) [24,25]		
	Recovery	LoD	LoQ	Recovery	LoD	LoQ	Recovery	LoD	LoQ
Nap	112	12.2	20.7	97	14.7	28.7	103	3.3	6.0
Acy	81	2.1	5.0	124	1.4	5.2	103	1.3	3.7
Ace	101	10.3	27.8	116	0.4	2.2	103	0.3	0.6
Flu	82	14.4	32.7	122	1.2	3.9	104	0.2	0.4
Phe	102	2.8	6.4	118	0.7	3.8	113	1.4	3.4
Ant	109	7.1	16.1	118	0.1	0.4	106	0.9	1.7
Flur	98	9.5	15.5	123	0.7	2.4	107	0.4	0.7
Pyr	107	13.5	25.0	123	0.5	1.5	103	0.05	0.1
B[*a*]A	107	2.1	4.6	115	0.6	1.8	106	0.2	0.2
Chr	120	2.9	6.4	122	0.7	2.0	101	0.1	0.2
B[*b*]F	92	0.2	0.4	105	1.4	4.7	107	0.5	0.8
B[*k*]F	92	0.2	0.5	108	0.9	2.5	115	0.5	1.0
B[*a*]P	85	0.4	0.7	120	4.1	11.3	97	0.4	0.6
D[*ah*]A	112	2.3	5.4	116	1.6	4.8	120	0.1	0.1
B[*ghi*]P	110	3.9	10.3	121	2.9	7.5	108	0.2	0.3
Ind	116	3.8	7.5	102	5.2	14.0	124	1.5	3.7
CB-18	90	25.5	64.6	121	3.2	9.3	80	0.1	0.3
CB-31	92	2.5	5.8	112	0.1	0.2	88	0.2	0.2
CB-28	81	1.5	3.4	127	0.05	0.2	90	0.3	0.7
CB-52	94	24.1	68.8	91	0.3	0.9	96	0.9	1.5
CB-44	87	4.6	12.2	110	0.2	0.6	98	0.1	0.3
CB-101	107	31.6	79.4	110	0.7	4.0	91	1.4	2.1
CB-153	119	2.3	4.3	102	0.6	2.2	84	0.8	0.8
CB-118	109	16.4	39.4	102	2.1	7.5	98	0.3	0.4
CB-138	120	2.1	4.6	108	0.3	1.1	92	0.7	1.4
CB-149	120	2.2	4.7	115	0.1	0.2	87	0.7	0.9
CB-180	91	0.6	1.5	120	0.1	0.6	82	0.2	0.5
CB-194	106	1.0	1.8	127	3.9	10.1	101	0.5	1.0
DMP	81	37.0	63.6	91	10.0	41.9	95	2.0	3.3
DEP	117	62.4	103.4	116	4.9	13.4	96	2.0	5.2
DBP	96	222	396.1	126	6.8	41.2	123	0.5	1.1
BBP	116	29.8	63.7	123	0.3	1.5	124	1.8	4.8
DEHP	116	252	475	107	5.1	16.2	109	0.1	0.1
DOP	96	105	232	116	0.1	0.6	101	2.2	4.4
NP	102	307	491	94	11.8	43.3	117	0.7	0.9
NP1EO + NP2EO	121	317	502	119	20.4	52.0	100	2.1	3.0
BDE-28	97	0.1	0.1	87	0.1	0.2	103	0.6	1.8
BDE-47	102	0.2	0.4	81	0.03	0.1	102	1.4	4.1
BDE-66	108	0.4	0.8	87	0.1	0.2	106	1.9	5.5
BDE-99	101	1.1	2.2	93	0.5	1.8	90	1.8	4.4
BDE-100	92	1.7	3.3	117	0.7	2.7	85	1.9	5.4
BDE-85	94	1.9	3.8	94	1.7	6.2	92	0.2	0.4
BDE-138	115	4.7	8.1	116	1.4	4.8	82	0.6	0.9
BDE-153	121	5.1	8.7	110	1.7	5.9	98	0.6	0.8
BDE-154	116	5.3	9.1	94	1.4	4.7	86	1.1	1.9
BB-7	96	0.9	1.9	110	0.1	0.3	102	0.4	1.0
BB-31	108	0.4	0.8	124	0.03	0.1	981	0.9	2.5
BB-103	121	1.7	3.6	106	0.4	1.3	83	3.5	9.8
BB-153	88	1.7	3.8	90	0.6	3.8	90	0.7	1.6

These results demonstrate the extremely high sensitivity of MASE-LVI-PTV-GC–MS and SBSE-TD-GC–MS procedures that allow the use of only 15–20 mL of samples to detect even the more restrictive maximum level of 10 ng L^{-1} of B[*a*]P and 100 ng L^{-1} as the sum of several PAHs (benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, indeno[1,2,3-*cd*]pyrene), as stated in the 98/83/EC European Directive for water for human consumption [38].

The precision was evaluated on relative chromatographic peak areas (with respect to internal standards) of 100 ng L^{-1} standard solutions ($n = 6$) which were analysed in the same day and by the same analyst in the case of both methods MASE-LVI-PTV-GC–MS (SIM) and SBSE-TD-GC–MS (SIM). RSD values within 3% and 19% were obtained within a day for all analytes and for both techniques. The RSD values obtained for PEs and NPs after the use of deuterated surrogates were similar to those obtained in a previous work where non-deuterated analogues were used [8].

Assays were performed on 100 mL spiked Milli-Q water (containing a 20% of methanol) at 100 ng L^{-1} concentration level for the analytes. Subsequently, different aliquots ($n = 6$) were extracted and analysed by MASE-LVI-PTV-GC–MS (SIM) and SBSE-TD-GC–MS (SIM) under optimised experimental conditions in order to calculate the extraction yields.

Similar and good recoveries were obtained in the case of MASE (81–121%) and SBSE (81–126%) procedures (see Table 6). It should be underlined that methanol should be added as soon as possible in the sampling step in order to avoid adsorption of the analytes in the sampling bottle [27,29].

3.5. Application of the developed methods to real samples

The applicability of SBSE and MASE to environmental samples was studied by applying the optimised extraction methods to three environmental water samples of natural seawater, Getxo (43°20′19.90″N, 3°0′54.07″W) and estuarine water, Udondo (43°18′45.08″N, 2°59′19.53″W) and Lamiako (43°19′8.71″N, 3°0′24.64″W) from the estuary of Bilbao (Northern Spain).

Table 7
Average concentrations ($n=4$) (ng L^{-1}) and standard deviations obtained in the analysis of real samples from Udondo (estuarine water), Lamiako (estuarine water) and Getxo (seawater).

Compound	Udondo		Getxo		Lamiako	
	MASE[a]	SBSE[a]	MASE[a]	SBSE[a]	MASE[a]	SBSE[a]
Nap	119 ± 16	101 ± 2	166 ± 25	160 ± 5	141 ± 23	188 ± 11
Acy	168 ± 12	152 ± 7	92 ± 3	82 ± 4	217 ± 4	193 ± 1
Ace	68 ± 13	72 ± 11	110 ± 6	96 ± 5	111 ± 7	105 ± 4
Flu	–	22 ± 1	37 ± 4	40 ± 3	56 ± 4	77 ± 3
Phe	38 ± 3	34 ± 3	118 ± 20	102 ± 3	144 ± 4	116 ± 2
Ant	18 ± 2	17 ± 3	76 ± 12	74 ± 3	107 ± 3	105 ± 2
Flur	–[b]	–	21 ± 2	20 ± 1	24 ± 4	30 ± 1
Pyr	–	–	30 ± 2	30 ± 1	29 ± 1	39 ± 1
B[*a*]A	–	1.9 ± 0.2	n.d.[c]	n.d.	n.d.	n.d.
Chr	–	–	n.d.	n.d.	n.d.	n.d.
B[*b*]F	n.d.[c]	n.d.	9 ± 1	12 ± 1	21 ± 2	11 ± 1
B[*k*]F	40 ± 4	36 ± 3	10.1 ± 0.1	8.4 ± 0.2	18 ± 2	12 ± 1
B[*a*]P	n.d.	n.d.	9.7 ± 0.5	11.0 ± 0.2	23 ± 3	25 ± 1
D[*ah*]A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
B[*ghi*]P	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ind	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ΣPAHs	451 ± 50	437 ± 30	679 ± 76	635 ± 27	891 ± 57	901 ± 28
CB-18	–	23 ± 4	n.d.	n.d.	n.d.	n.d.
CB-31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CB-28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CB-52	75 ± 5	71 ± 7	–	16 ± 2	–	34 ± 5
CB-44	n.d.	n.d.	9 ± 2	8 ± 1	24 ± 2	26 ± 3
CB-101	149 ± 3	140 ± 14	–	60 ± 2	220 ± 24	207 ± 13
CB-153	18 ± 1	25 ± 3	7 ± 1	5 ± 1	19 ± 2	26 ± 1
CB-118	86 ± 5	77 ± 5	44 ± 9	52 ± 3	133 ± 6	132 ± 9
CB-138	6 ± 1	10 ± 2	–	3.4 ± 0.2	n.d.	n.d.
CB-149	15 ± 1	n.d.	6 ± 1	5.7 ± 0.2	16 ± 1	24 ± 3
CB-180	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CB-194	8 ± 1	11 ± 2	n.d.	n.d.	n.d.	n.d.
ΣPCBs	357 ± 17	357 ± 37	91 ± 13	150 ± 10	412 ± 35	449 ± 34
DMP	301 ± 12	267 ± 24	248 ± 40	223 ± 12	209 ± 26	279 ± 25
DEP	–	92 ± 10	–	43 ± 2	–	66 ± 9
DBP	453 ± 17	424 ± 13	397 ± 74	249 ± 2	1259 ± 117	1253 ± 100
BBP	–	52 ± 3	–	62 ± 1	–	46 ± 2
DEHP	–	232 ± 19	–	166 ± 7	–	215 ± 10
DOP	–	34 ± 4	–	30 ± 2	–	32 ± 2
ΣPEs	754 ± 29	1101 ± 73	645 ± 114	773 ± 26	1468 ± 143	1891 ± 148
NP	–	–	–	321 ± 10	–	155 ± 10
NP2EO + NP2EO	–	–	–	125 ± 5	–	175 ± 5
BDE-28	n.d.	n.d.	n.d.	n.d.	21 ± 1	19 ± 1
BDE-47	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-66	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-99	114 ± 13	123 ± 8	46 ± 9	54 ± 5	n.d.	n.d.
BDE-100	37 ± 2	38 ± 8	23 ± 2	36 ± 2	90 ± 3	78 ± 10
BDE-85	183 ± 17	160 ± 17	214 ± 14	223 ± 21	201 ± 13	181 ± 11
BDE-138	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-153	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
BDE-154	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
ΣPBDEs	334 ± 32	321 ± 33	283 ± 25	313 ± 32	312 ± 17	278 ± 21

[a] Technique.
[b] <LoD.
[c] Not detected compound.

The average concentration ($n=4$) obtained for all the analytes with their corresponding uncertainties are shown in Table 7. It should be underlined that the presence of organic matter was not taken into account in the calculation of those values and, thus, those concentrations should be considered as the free fraction of the analytes not bound to organic matter [24,25].

As it can be observed from the data in Table 7, comparable concentrations were estimated in the three sampling points and for the six families of analytes except for PEs and NPs in Getxo and NPEOs in Lamiako. PBBs congeners were not detected in any of the samples analysed no matter which preconcentration technique was used.

4. Conclusions

SBSE followed by TD-GC–MS and MASE combined with LVI-PTV-GC–MS have been successfully applied for the simultaneous determination of PAHs, PCBs, PBDEs, PBBs, PEs, NPs and NPEOs in water samples. In general, the SBSE method provided better LoD

values, whereas MASE resulted in similar recoveries, but faster extraction.

Polypropylene membranes have also the advantage of the low cost and easy handling. Due to the composition of the membrane material, however, a thorough cleaning procedure for the membranes is necessary in order to improve the LoDs in the case of PEs and NPs.

The results of water samples obtained by both methodologies were comparable, indicating that these efficient and environmentally friendly analytical procedures can be employed for the determination of a wide range of priority organic contaminants found in water samples. The comparable concentrations obtained validate the optimised preconcentration procedures.

Acknowledgements

This work has been economically supported through the UNESCO 07/09 project financed by the University of Basque Country and the CTM 2006-13880-C03-02/MAR project founded by the Spanish Ministry of Science and Technology.

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