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Simultaneous determination of 76 micropollutants in water samples by headspace solid phase microextraction and gas chromatography–mass spectrometry

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ABSTRACT

This study focuses on the development of an analytical method based on headspace solid phase microextraction (HS-SPME) and gas chromatography–mass spectrometry (GC–MS) for the simultaneous determination of 76 micropollutants in water samples. The selected micropollutants include volatile organic compounds (VOCs) (e.g. chlorobenzenes, chloroalkanes), endocrine disrupting compounds (EDCs) (e.g. bisphenol A and tributyl phosphate), odour compounds (e.g. limonene, phenol), fragrance allergens (e.g. geraniol, eugenol) and some pesticides (e.g. heptachlor, terbutryn). The experimental conditions affecting their extraction, such as the type of fibre, temperature and time of extraction, sample volume and ionic strength of the samples were optimized using HS-SPME. The method showed good linear range, reproducibility between days, repeatability and low detection limits (at ng L^{-1} levels). The validated method has been applied to determine the target organic micropollutants in aqueous samples from different experimental research units of surface water, sea water, waste water and those effluents of advance membrane treatments. The optimized method showed good performance in the different types of samples studied. The analysis revealed the presence of several micropollutants at concentrations between 20 and 5000 μg L^{-1}, such as ethylbenzene, o-xylene, p-isopropilbenzene, D-limonene, citral and isoeugenol, due to the fact that these species are commonly used in domestic and industrial applications.

1. Introduction

Contamination of environmental waters by trace levels of organic substances, called organic micropollutants, is a subject of increasing concern in the majority of countries. The organic micropollutants includes any organic compounds that may be found at microgram per litre concentrations or lower in water, such as pesticides, pharmaceutical residues, hormones, flame-retardants, plasticizers, perfluorinated compounds, among others [1].

Water quality is currently controlled by several legislations. For instance, the United States Environmental Protection Agency (U.S. EPA) has developed classification systems and Environmental Quality Standards (EQS) for assessing the quality of surface waters [2]. Moreover, in the European Union, the Water Framework Directive, Directive 2008/105/CE control the river, lake, ground and coastal waters and also heavily modified and artificial water bodies [3]. These regulations limit some of the micropollutants studied at low levels of concentration (μg L^{-1}) in order to prevent further deterioration and protect, enhance and restore the status of all bodies of water with the aim of achieving at least good status by 2015. Nevertheless, occurrences in groundwater and drinking waters of some other unregulated substances have also been reported in the literature [4].

However, the low levels of micropollutants in waters and the high complexity of water samples require the development of highly sensitive and selective analytical methods that can simultaneously determine a broad range of these pollutants. For the present work, different families of micropollutants were selected and described below.

Volatile organic compounds are one of the chief issues in the environment. VOCs have neurotoxic and genotoxic effects on human health and can cause respiratory and reproductive disorders [5]. Moreover, they represent approximately 10% of the total dissolved organic carbon of unpolluted waters and the

Abbreviations: EDCs, endocrine disrupting compounds; EDSP, endocrine disruptor screening program; EPA, environmental protection agency; EQS, environmental quality standards; GC–MS, gas chromatography–mass spectrometry; HS-SPME, headspace solid phase microextraction; LOD, limit of detection; LOQ, limit of quantification; PDMS, polydimethylsiloxane; PDMS/DVB, polydimethylsiloxane/divinylbenzene; PDMS/DVB/CAR, polydimethylsiloxane/divinylbenzene/carboxen; RO, reverse osmosis; SPE, solid phase extraction; UF, ultrafiltration; VOCs, volatile organic compounds

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concentrations are much higher in raw waters from different anthropogenic sources [6]. In this study 52 VOCs have been selected, being some of them regulated by the Directive 2008/105/CE.

Endocrine disrupting compounds (EDCs) are chemicals which have the potential to disturb hormonal equilibrium in living organisms [7]. These compounds, mistakenly recognized by estrogenic receptors, are treated the same as those naturally present in the organisms. Many EDCs are not regulated yet. However, with the collection of sufficient data to prove their toxic effects on human health, they may be the most probable target compounds for future regulation [8]. The U.S. EPA tried to establish the Endocrine Disruptor Screening Program (EDSP) to develop official screening methods and toxicity testing strategies for approximately 87.000 compounds [9]. In this study 3 EDCs have been selected.

Odour emissions affect quality of life, leading to psychological stress and symptoms such as insomnia, loss of appetite and irrational behaviour [10,11]. Therefore, waste water professionals have found the need to address odours as a primary concern in the design and operation of collection and treatment facilities in order to control odour emissions. However, there is no any European legislation that controls odour compounds in waters. Thus, the most commonly odour compounds detected in the waters (eight) were selected to be analyzed.

Fragrance allergens are a group of chemicals incorporated in most cosmetic and other personal care products including baby care ones. Some of the suspected allergens can cause systemic effects. Legal restrictions only limit the use of 26 fragrance ingredients suspected of causing skin reactions [12–14]. In this study, ten of these fragrances have been selected, which are reported as the most allergens.

The last group of selected compounds has been some pesticides which were proposed for regulation by the European Commission, on the 31st of June of 2012 [15]. They are generally toxic for living organisms and are difficult to degrade, being toxic agents with persistent bioaccumulative effects [16]. In this study three of these pesticides have been selected.

As the demand for high-quality water is constantly increasing through the world, many studies have given considerable attention aimed at establishing the removal efficiency of organic solutes. Some trends on advance treatments are based on advanced membrane treatments, such as reverse osmosis (RO). Since the development of reverse osmosis and ultrafiltration (UF) as a practical unit operation in the late 1950's, the scope for their application has been continually expanding. In general, RO membranes now offer the possibility of higher rejection of inorganic and organic compounds, including micropollutants. Moreover, UF processes are used as a pretreatment of the reverse osmosis, improving the efficiency of these advance treatments. A few actual studies can be found evaluating the elimination of drugs of abuse, endocrine disrupting compounds, pharmaceuticals and personal care products [17–20].

Several extraction techniques can be used for the extraction of organic micropollutants from water samples, whereas solid phase microextraction has been used as the best option for these compounds, while it can selectively extract selected compounds and no solvents are required [21–23]. SPME allows complete elimination of organic solvents in the pretreatment step and decreasing the steps for sample preparation and has become an accepted method for the determination of volatile and semi-volatile substances. Therefore, in this study headspace solid phase microextraction (HS-SPME) has been used for the determination of the organic micropollutants in water, due to its advantages. The advantage of HS techniques when volatile compounds are analyzed is that the extraction is more selective and the matrix influence becomes lower [11].

In this study a method based on HS-SPME and GC–MS for the characterization of 76 compounds belonging to different chemical families has been developed. The method has been applied for determine the micropollutants in water samples, which are natural water samples coming from river, wastewater treatment plant and sea. To allow the study of removal of priority compounds by membrane systems, a cost-effective screening technique was developed, which does not use solvent and allows characterization of a large variety of compounds simultaneously.

2. Experimental

2.1. Chemical and reagents

The 54 volatile organic compounds were obtained from a mixture of 592/524 Volatile Organics Calibration Mix, EPA 524.2 provided by Sigma-Aldrich, Supelco (Madrid, Spain), all of them in a concentration of 2000 mgL^{-1} in methanol. Standard solution of Geosmin (100 mg L^{-1} in methanol), was also supplied by Sigma-Aldrich.

Individual standards of fragrance allergens: benzyl alcohol, citral, geraniol, hydroxycitronellal, cinnamyl alcohol, eugenol, amyl cinnamaldehid and benzyl salicycate were supplied by Sigma-Aldrich. Moreover, coumarin and isoeugenol analytical standards were provided by Dr. Ehrenstorfer (Augsburg, Germany). Individual standards of odours compounds: dimethyl disulfide, limone, carvone and skatole were supplied by Sigma-Aldrich. Furthermore, 3-methylphenol, phenol and indole analytical standards were supplied from Dr. Ehrenstorfer. Individual standards of pesticide compounds: heptachlor, terbutryn and dicofol were provided by Sigma-Aldrich. Individual standards of EDCs compounds: bisphenol A, tris(2-chloroethyl) phosphate and tributyl phosphate were also supplied from Sigma-Aldrich.

Four solution mixtures of the different families of compounds (odours, allergens, EDCs and pesticides) were prepared at 2000 mg L^{-1} in methanol from the individual standards. A standard mixture solution of 75 compounds was prepared from the solutions described above (100 mg L^{-1} in methanol), except for geosmin which was purchased directly at 100 mg L^{-1}. Working solutions were prepared daily in methanol GC grade with purity $>$ 99.9% (from Prolabo, Barcelona, Spain) and stored under refrigeration (2–6°C). The minimal purity of the standards was 98%.

Sodium chloride (NaCl) (ACS reagent≥99%) was supplied by Sigma-Aldrich. Helium gas 99,999% was supplied from Praxair, Barcelona, Spain.

Three commercial extraction fibres including 100 μm Polydimethylsiloxane (PDMS), 65 μm Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) and 50/30 μm Polydimethylsiloxane/Divinylbenzene/Carboxen (PDMS/DVB/CAR) were purchased from Supelco.

2.2. Sample collection

The analytical method has been developed to analyze different types of water samples. Studied samples belong to the inlet and outlet of tertiary advanced membrane treatments. The inlet is called influent and the outlet, effluent. These treatments are applied using research units, which are big pilot plants of ultrafiltration and reverse osmosis processes, located in real installations.

The water treated ranged from surface water (Llobregat River, Barcelona, Spain), effluents of secondary treatment of an urban waste water treatment plant (Vila-Seca, Spain) and sea water (Mediterranean Sea, Tarragona, Spain). Seawater and river water are treated with a plant according to Fig. 1A while wastewater is treated with a plant according to Fig. 1B. The process and sampling points (stars) are shown schematically, also in Fig. 1; sea water and

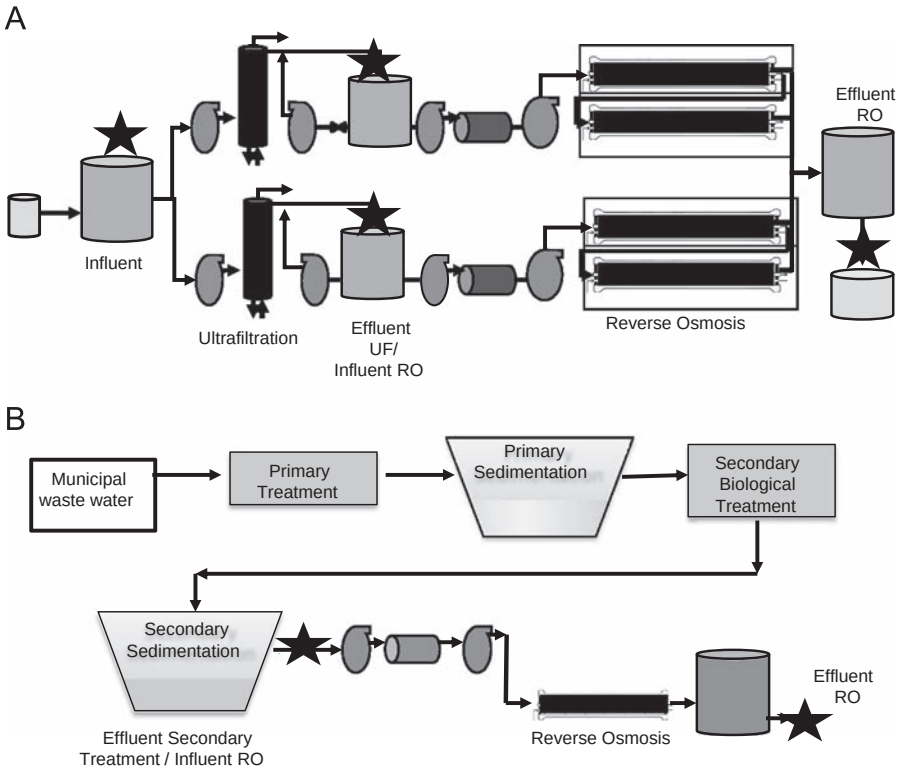

Fig. 1. (A) Sea water and surface water application research units with ultrafiltration and reverse osmosis processes with stars as a sample points in black, and (B) waste water treatment plant from Vila-Seca with application research units of reverse osmosis membranes as a tertiary treatment with stars as a sample points in black.

surface water application research units with ultrafiltration and reverse osmosis processes, waste water treatment plant with a water application research unit of reverse osmosis membranes as a tertiary treatment.

Samples were taken on August of 2012. Water samples were collected in amber glass containers and were stored in the dark at 4 °C until analysis, within two days.

2.3. Headspace-solid phase microextraction equipment

For the extraction procedure, 30 mL of sample was introduced into a 50 mL PTFE/silicone screw-cap glass vial. Then, 0.4 g mL^{-1} of NaCl (saturated solution) was added; the vial was closed and put over a magnetic stirrer in a water thermostatic bath at 50 °C. The magnetic stirring was applied at 1000 rpm during the 30 min of extraction and the fibre of PDMS/DVB was exposed to the headspace above the aqueous solution. After the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 270 °C during the chromatographic analysis in the splitless mode. Blanks of the fibres needed to be analyzed before a sample gets extracted.

2.4. Gas chromatography–mass spectrometry equipment and experimental conditions

The gas chromatography analysis was performed with a GCMS-QP2010 Ultra/ GCMS-QP2010 SE from Shimadzu, equipped with a split/splitless injector and coupled to a mass spectrometer detector. Helium was employed as a carrier gas at constant column flow of 1 mL min^{-1}. Analytes were separated with TRB-5MS column (60 m × 0.32 mm i.d., 1 μm film thickness) from Tecknokroma, Barcelona, Spain. The split/splitless injection port was equipped with a 0.75 mm ID liner from Supelco, and operated at 270 °C, allowing direct injection or SPME. The oven temperature program was started at 40 °C, held for 2 min; then increased by 6 °C min^{-1} up to 150 °C and by 20 °C min^{-1} up to 300 C°, and held for 12 min. The total run was 39 min. The MS analyses were conducted in full-scan mode with a single quadrupole and monitored masses between 40 and 280 m/z. Ionization was carried out in the electron impact (EI) mode at 70 eV. The transfer line temperature was maintained at 300 °C and the ion source temperature at 250 °C.

3. Results and discussion

3.1. GC–MS optimization

A method for the simultaneous determination of 76 micropollutants has been developed. The chromatographic separation takes 39 min. To optimize the chromatographic separation, individual mixtures of the different families of the micropollutants were injected in order to separate each compound appropriately. Then, 1 μL of 10 mg L^{-1} mixture of all micropollutants was directly injected in the splitless injector in Full-scan mode. After the optimization of the temperature gradient, the retention time of every compound was determined. Moreover, the quantification ion of each compound was selected, which are summarized in Table 1. Then, two qualification ions were selected for each compound, presented in Table 1 and compound confirmation was done with whole mass spectrum.

3.2. HS-SPME optimization

Optimization of solid-phase microextraction conditions for the 76 micropollutants selected was accomplished using aliquots of effluents of application research units of reverse osmosis of surface water spiked with the analytes at 0.33 μg L^{-1} level ($n=3$). According to recent literature [24,25], the parameters predicted to

Table 1
Target compounds, quantification and identification ions and main validation data obtained by analyzing effluents of reverse osmosis of surface water spiked at 1 ng mL^{-1} ($n=5$).

Family	Compound	t_R (min)	Quantification ions	Identification ions	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	r^2	RSD[A] (%)	RSD[B] (%)
VOCs	1.1-dichloroethene	5.17	61	96, 98	0.100	0.333	0.989	4.7	8.2
	(Z)-1.2-dichloroethene	6.35	61	96, 63	0.033	0.100	0.990	5.2	6.1
	1.1-dichloroethane	6.40	63	65, 83	0.033	0.333	0.997	3.6	5.6
	2.2-dichloropropane	6.60	77	79, 97	0.033	0.100	0.990	7.8	7.5
	Trichloromethane[a]	6.67	83	85, 47	0.001	0.003	0.989	4.5	8.2
	(E)-1.2-dichloroethene	7.16	61	96, 63	0.033	0.333	0.988	9.8	8.7
	Bromochloromethane	7.41	130	128, 93	0.100	0.333	0.988	20.3	18.3
	1.1.1-trichloroethane	7.69	97	99, 61	0.033	0.333	0.993	5.3	6.9
	1.2-dichloroethane	7.74	62	64, 49	0.033	0.333	0.993	4.2	7.3
	1.1-dichloro-1-propene	8.05	75	39, 110	0.017	0.033	0.992	5.6	8.3
	Benzene	8.26	78	51, 52	0.001	0.003	0.997	4.3	8.7
	Carbon tetrachloride	8.38	117	119, 121	0.003	0.033	0.993	6.4	10.1
	1.2-dichloropropane	9.44	63	62, 76	0.017	0.033	0.998	4.3	5.2
	Trichloroethene	9.59	130	95, 132	0.003	0.033	0.991	5.2	11.3
	Dibromomethane[a]	9.78	174	172, 93	0.003	0.033	0.992	3.2	5.2
	Bromodichloromethane[a]	10.11	83	85, 129	0.100	0.333	0.987	18.9	20.5
	(E)-1.3-dichloro-1-propene	11.14	75	39, 110	0.001	0.003	0.999	5.5	10.1
	(Z)-1.3-dichloro-1-propene	11.65	75	39, 110	0.003	0.010	0.993	6.1	10.9
	Toluene	12.13	91	92	0.0005	0.002	0.991	7.5	12.3
	1.1.2-trichloroethane	12.23	97	83, 61	0.100	0.333	0.988	17.3	15.7
	1.3-dichloropropane	12.64	76	41, 78	0.010	0.033	0.994	4.7	8.3
	Dibromochloromethane[a]	13.12	129	127, 131	0.001	0.003	0.992	7.8	9.2
	1.2-dibromoethane	13.49	107	109	0.017	0.033	0.997	10.2	13.6
	Tetrachloroethene	13.62	166	164, 129, 131	0.033	0.333	0.992	2.8	5.1
	Chlorobenzene[a]	14.85	112	77, 114, 51	0.001	0.033	0.992	3.1	4.2
	1.1.1.2-tetrachloroethane	14.92	131	133, 117, 119	0.010	0.033	0.999	8.2	9.8
	Ethylbenzene[a]	15.31	91	106	0.0005	0.002	0.993	6.9	12.6
	o-Xylene[a]	15.56	91	106, 105, 77	0.001	0.003	0.994	8.7	11.3
	Tribromomethane[a]	16.17	173	93, 81	0.100	0.333	0.978	21.2	20.8
	Styrene	16.27	104	78, 103	0.0005	0.002	0.998	5.7	7.7
	p-Xylene/m-xylene[a]	16.38	91	106, 105	0.0005	0.002	0.994	5.8	8.0
	1.1.2.2-tetrachloroethane	16.83	83	85, 95, 131	0.010	0.033	0.998	6.2	7.2
VOCs	1.2.3-trichloropropane	17.10	75	97, 110	0.010	0.033	0.996	5.1	6.3
	Isopropilbenzene[a]	17.35	105	120, 79	0.001	0.003	0.999	8.2	12.5
	Bromobenzene	17.71	77	156, 158, 51	0.0005	0.003	0.999	9.1	10.4
	1-chloro-2-methylbenzene	18.32	126	125, 128	0.001	0.003	0.998	8.3	10.2
	1-chloro-4-methylbenzene	18.47	91	126, 125	0.010	0.033	0.996	6.2	8.8
	1.2.4-trimethylbenzene	18.72	105	120	0.0005	0.002	0.998	11.3	13.2
	1.3.5-trimethylbenzene	18.95	105	120	0.010	0.033	0.998	11.6	6.2
	Tert-butylbenzene	19.52	119	91, 134	0.0005	0.002	0.999	5.2	7.3
	Sec-Butylbenzene	20.07	105	134	0.0005	0.002	0.999	3.9	6.8
	1.3-dichlorobenzene	20.20	146	148, 111, 75	0.010	0.033	0.991	7.3	11.8
	p-Isopropilbenzene	20.43	119	91, 134	0.0005	0.002	0.998	7.8	9.8
	1.2-dichlorobenzene	20.92	146	148, 111	0.001	0.003	0.993	7.2	9.8
	1.4-dichlorobenzene	21.02	146	148, 111, 75	0.010	0.033	0.993	10.3	10.5
	Butylbenzene	21.30	91	92, 134	0.0005	0.002	0.997	5.6	11.7
	1.2-dibromo-3-chloropropane	22.05	157	155, 75	0.001	0.003	0.997	6.2	7.3
	1.2.4-trichlorobenzene	23.95	180	182, 145	0.001	0.003	0.991	4.2	8.9
	Naphthalene	24.14	128	127, 129	0.0005	0.003	0.998	7.8	12.1
	Hexachlorobutadiene	24.52	225	227, 223	0.010	0.033	0.991	8.5	7.1
	1.2.3-trichlorobenzene	24.55	180	182, 145	0.010	0.033	0.990	12.3	8.9
Odours	Dimethyl disulfide	11.40	94	79, 45	0.017	0.033	0.998	5.9	11.5
	Phenol	18.62	94	66	0.001	0.333	0.989	25.3	10.1

	D-limonene[a]	20.60	68	93	0.001	0.003	0.999	9.2	10.3
	3-methyl-phenol	21.40	108	107, 79	0.100	0.333	0.991	6.3	14.8
	Carvone[a]	24.81	82	54, 108	0.001	0.003	0.993	11.8	13.6
	Indole	25.48	117	90	0.100	0.333	0.991	9.7	9.3
	Skatole	26.56	130	131, 77	0.010	0.033	0.993	4.4	10.4
	Geosmin	26.98	112	125, 97	0.0005	0.002	0.997	2.8	8.6
Allergens	**Benzyl alcohol**	20.54	79	108	0.001	0.003	0.989	9.8	12.4
	Citral	24.62	41	69	0.010	0.033	0.993	8.2	10.2
	Geraniol	24.72	69	41	0.033	0.100	0.990	13.1	15.2
	Hidroxicitronellal	25.16	59	43, 71	0.100	0.333	0.992	5.2	7.9
	Cinnamyl alcohol	25.84	92	78, 134	0.100	0.333	0.997	18.8	19.6
	Eugenol	26.12	164	103	0.010	0.033	0.993	3.7	7.7
	Isoeugenol	27.04	164	149	0.100	0.333	0.991	15.6	12.3
	Coumarin[a]	27.18	118	146, 90	0.0005	0.002	0.988	14.2	18.9
	Ammylcinamaldehid	28.67	129	91, 117	0.0005	0.002	0.996	15.1	11.6
	Benzil salizicate	30.49	91	65	0.017	0.060	0.990	12.9	11.2
Pesticides	**Terbutryn**	30.87	226	241, 170	0.010	0.033	0.995	10.1	13.8
	Heptachlor	31.17	100	272	0.017	0.060	0.991	9.9	6.3
	Dicofol	31.64	139	111, 251	0.017	0.060	0.995	8.3	14.3
EDCs	**Tributyl phosphate**[a]	28.37	99	155, 211	0.001	0.003	0.999	5.3	7.2
	Tri(2-chloroethyl) phosphate	29.35	63	249	0.001	0.003	0.993	21.2	22.8
	Bisphenol A	33.23	213	119, 228	0.001	0.003	0.986	13.5	18.2

A: Repeatability. B: Reproducibility.

[a] Compounds found in reverse osmosis effluents.

affect the extraction are: type of fibre, extraction temperature, ionic strength, extraction time and sample volume. The optimization was carried out by comparing the chromatographic areas of the compounds analyzed at different conditions.

Initial extraction conditions were: 20 mL of sample (described above) was introduced into a 50 mL PTFE/silicone screw-cap glass vial. Then, 0.4 g mL^{-1} of NaCl (saturated solution) was added, the vial was closed and put over a magnetic stirrer in a water thermostatic bath at 50 °C. The magnetic stirring was applied at 1000 rpm during the 30 min of extraction and the fibre was exposed to the headspace above the aqueous solution. After the extraction, the fibre was inserted into the injection port of the gas chromatograph for the thermal desorption and analysis. Fibre was desorbed at 270 °C during the chromatographic analysis in the splitless mode. Under these conditions, three replicates were done ($n=3$).

Due to the different properties of the compounds studied, three fibre coatings (PDMS, PDMS/DVB and PDMS/DVB/CAR) were selected for evaluation. In this study, differences between the three coatings in terms of area were observed. Fig. 2(A), shows the behaviour of the different families of the compounds selected. PDMS/DVB gave higher increased area for the majority of the target micropollutants, so it was selected as the best coating for the extraction of these micropollutants from the water.

Once the fibre coating was chosen, the best extraction temperature was studied. Higher extraction temperatures increase vapour pressure for volatile analytes in the headspace. However, higher temperatures might also create a less favourable coating-headspace (air) partition. To optimize the responses, extraction temperature was examined at these three different levels: 30 °C, 50 °C and 70 °C. Initial conditions were the same as above using the selected PDMS/DVB fibre. Fig. 2(B) shows the effect of temperature on the areas of the representative families of the compounds selected. Extraction efficiency for most of the target VOCs was higher at 30 °C whereas the rest of other families presented higher areas at 70 °C because of the chemical properties of the different micropollutants studied. An extraction temperature of 50 °C was selected for this study as a compromise between the results.

Responses of the micropollutants were also checked for 15, 30 and 45 min of extraction time. Initial conditions were described above. Fig. 2(C) shows the effect of extraction time on the responses of the representative families of compounds chosen above. The figure shows a trend where some components still increased their area after an extraction time of 45 min, however 30 min was the extraction time chosen in order to use a reasonable extraction time while obtaining a good compromise between sensitivity and time of analysis.

The effect of sample volume was evaluated using 20, 30 and 40 mL of sample in a 50 mL glass vial. Results of the sample volume influence are shown in Fig. 2(D). As observed, the preferred sample volume for the different families of compounds was 30 mL of water sample.

The ionic strength of the sample had a positive effect on the extraction of all the studied compounds. The suitability of the HS-SPME technique for the extraction compounds from water depends on the transfer of the analyte from the aqueous phase to the gaseous phase. This effect depends on the polarity of the analyte, the concentration of salt and the sample matrix. The ionic strength test was performed using the initial conditions and the PDMS/DVB fibre at an extraction temperature of 50 °C. The effect of ionic strength was evaluated with the addition of 0; 0.2; 0.3 and 0.4 g mL^{-1} of NaCl. Fig. 2(E) shows the salting out effect on the areas of the representative families of the micropollutants selected. The responses for most target micropollutants increased with the addition of NaCl. Therefore, a concentration of 0.4 g mL^{-1} of NaCl (saturated solution) has been selected because the results showed highest response.

To summarize, optimized extraction conditions in this study were: headspace in a 50 mL vial, PDMS/DVB fibre, temperature 50 °C, 0.4 g mL^{-1} of NaCl addition, 30 min of extraction time, 30 mL sample volume, stirring at 1000 rpm and finally desorption of the fibres at 270 °C during the whole time of analysis. An exception occurs on sea water samples because of its content of salt. In this case, the addition of the sodium chloride was 10 g in 30 mL.

3.3. Method validation

The method has been validated with effluent of reverse osmosis from surface water treatment plant. Previous to the validation parameters, a sample of effluent was analyzed and some of the target compounds were identified (these compounds are marked with an asterisk in Table 1). Therefore, the average responses ($n=5$) of these compounds were considered when validation parameters were calculated.

Linear range of SPME procedure was investigated with increasing concentrations of the analytes at six different concentration levels from 0.002 to 5.000 μg L^{-1}. Each concentration level was analyzed in triplicate. An acceptable linear range, with determination coefficients (r^2) higher than 0.991, was obtained for the majority of compounds within this interval. Table 1 also shows the validation data. No saturation effect of the fibre has been observed at the described concentration range.

The limits of detection (LODs) of the compounds that did not appear in the samples were defined as the concentrations giving a response corresponding to a signal-to-noise ratio 3:1. The LODs of the compounds that appeared in the samples were estimated as the concentration that gave a signal average of plus three times the standard deviation of the sample signal.

LODs ranged from 0.0005 μg L^{-1} up to 0.100 μg L^{-1}, which are in agreement with those papers found in the literature [6,16,27] for VOCs, pesticides and allergens but are slightly lower for endocrine disruptor and odour compounds [11,26].

Limits of quantification (LOQs) were defined as the concentrations giving a response corresponding to a signal-to-noise ratio 10:1 but they were fixed as the lowest calibration level in order to assure correct quantification. LOQ ranged from 0.002 μg L^{-1} up to 0.333 μg L^{-1}.

The precision of the method was evaluated by spiking three replicates of a sample at 1 μg L^{-1} levels. Repeatability and reproducibility between 5 days were calculated as the percentage of the relative standard deviation ($n=5$), and were mostly lower than 20%.

In order to evaluate an estimated accuracy, the different water samples were also spiked at three different concentration levels (at 0.3 μg L^{-1}, 1 μg L^{-1} and 5 μg L^{-1}). For these three levels, the calculated concentrations of the target micropollutants were in agreement with those obtained with reverse osmosis effluents, taking into account the repeatability of the method used.

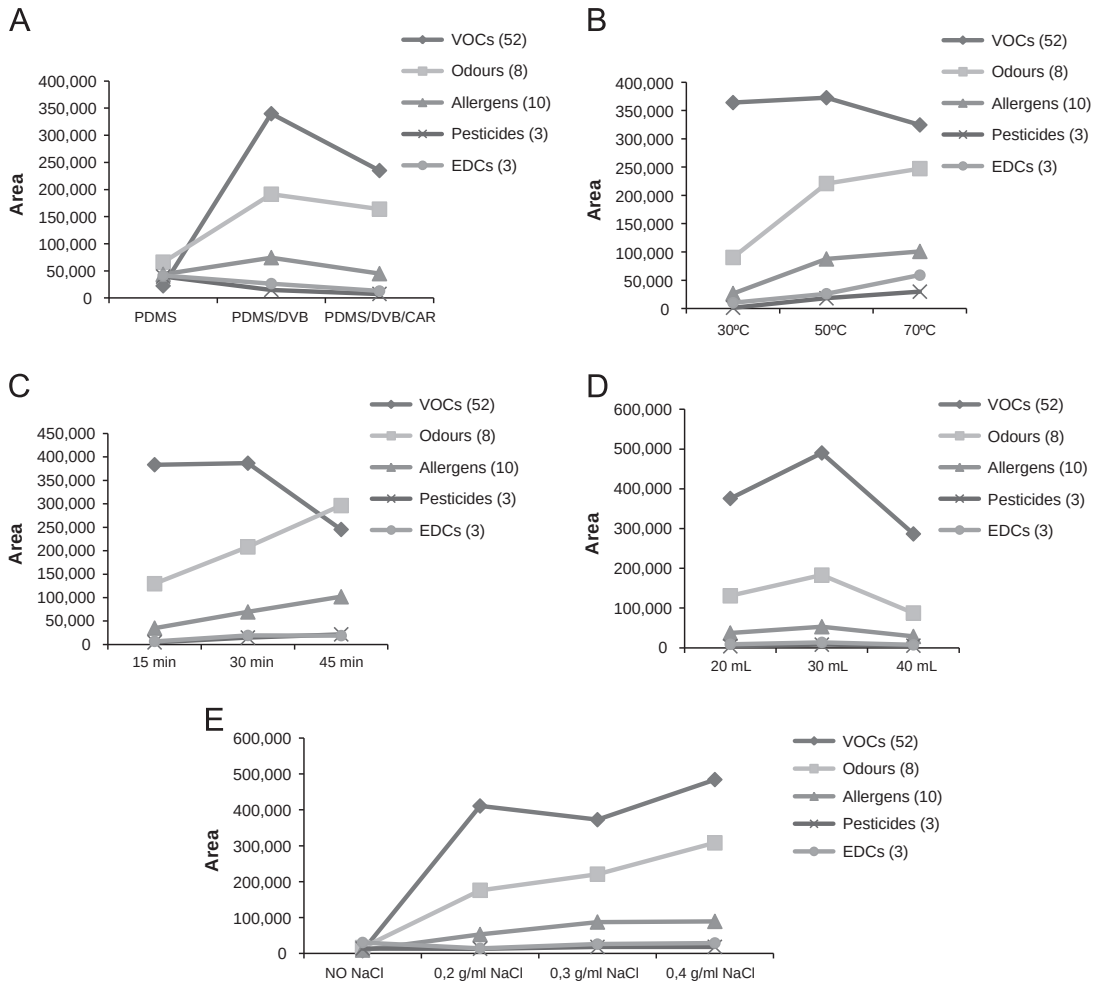

Fig. 2. Effects of fibre coatings (A), extraction temperature (B), extraction time (C), sample volume (D) and salting out effect (E) on the HS-SPME of different families (number of compounds in parenthesis) of micropollutants studied in effluents of RO water ($n=3$).

Quantification of the samples was performed by external calibration using the calibration curves obtained by spiking the standards in reverse osmosis effluent water. Exceptionally, waste water influent and effluent samples of reverse osmosis treatment presented matrix effect and were quantified with matrix match calibration line. Therefore, the quantification of these samples was performed using calibration curves obtained by spiking the standards in those waste water influent and effluent samples of reverse osmosis. Suspended matter or solids can have a significant influence on response at trace level analysis, in particular for influent samples.

3.4. Application of the method

By the proposed method, a total of 27 of the 76 micropollutants were detected and quantified in the different samples. As expected, the levels found in the influents of application research units of river water and seawater samples were considerably lower than those found in the influents of application research units of reverse osmosis of waste water. However, some of the influents contained higher values of micropollutants than their effluents because the hydraulic residence time has not been taken into account. Table 2 shows the concentration of the micropollutants found in all studied samples, influents and effluents of the plants that use a tertiary treatment with advanced membrane treatments such as UF and RO. The relative standard deviations were less than 15% for the concentrations up to 0.05 μg L^{-1} ($n=5$). Those target compounds not found in any type of samples studied are not included in Table 2.

The presence of 14 volatile organic compounds has been observed in effluents of secondary treatment of waste water samples. Eleven of them were also found in RO effluents of the application research units. Fig. 3 shows a chromatogram of two samples of the application research units of reverse osmosis membranes in the waste water treatment plant (WWTP), one of them is from the influent of RO and the other belongs to the effluent of RO. As expected, the influent sample contains more compounds than the effluent sample and it was seen that the majority of the compounds were reduced by using RO membrane treatments due to the capacity of these advance tertiary treatments to eliminate the organic compounds.

Moreover, some of the VOCs have been found in the influents of the application research units of sea water and surface water, at higher concentrations than in waste water secondary effluents. For instance, concentrations of tetrachloroethene, chlorobenzene and tribromomethane exceeded the linear range. Sea water and surface water analyzed in the application research units contained chlorine as a prevention of biofouling. Therefore, some disinfection by products could be formed in these types of water samples.

Some fragrance allergens like citral, coumarin, cinnamyl alcohol, isoeugenol and geraniol were detected in effluents of secondary treatment of waste water samples due to the use of these compounds in personal care products. These results also confirmed those reported in some articles [26–30]. In the application research units of seawater and surface water fewer fragrance allergens were found, only citral and coumarin.

Limonene and phenol as odours were detected in the influents of application research units of sea water. Furthermore, limonene was also detected in effluents of secondary treatment of waste water samples. These odour compounds could be present in the air and then precipitated into the waters.

Finally, tributyl phosphate, an endocrine disrupting compound, was also detected in effluents of secondary treatment of waste water samples and in the influent of the application research

Table 2
Concentrations of the micropollutants found in different pilot plants of water samples studied. Expressed in ng mL^{-1} ($n=5$; RSD < 15% at concentrations > 0.05 ng mL^{-1}).

Compound	Waste water		Sea water			River water		
	Effluent secondary treatment	Effluent RO	Sea water	Effluent UF/influent RO	Effluent RO	River water	Effluent UF/influent RO	Effluent RO
1.2-dichloroethane	0.20	n.d.	n.d.	n.d.	n.d.	0.46	n.d.	n.d.
Dibromomethane	0.60	n.d.	< loq	0.75	n.d.	n.d.	n.d.	n.d.
Toluene	0.043	0.069	< loq	< loq	0.088	n.d.	n.d.	n.d.
1.1.2-trichloroethane	3.2	n.d.	n.d.	n.d.	n.d.	1.4	< loq	n.d.
Dibromochloromethane	0.14	0.11	< loq	1.35	n.d.	0.003	< loq	n.d.
Tetrachloroethene	n.d.	n.d.	14.8[a]	< loq	34[a]	7.2[a]	n.d.	n.d.
Chlorobenzene	n.d.	0.18	n.d.	n.d.	1.22	n.d.	n.d.	n.d.
Ethylbenzene	0.069	0.033	< loq	< loq	< loq	n.d.	n.d.	< loq
o-Xylene	0.086	0.045	< loq	< loq	< loq	n.d.	n.d.	n.d.
Tribromomethane	n.d.	0.18	8.7[a]	67[a]	< loq	< loq	n.d.	n.d.
Styrene	n.d.	n.d.	< loq	< loq	0.23	< loq	n.d.	n.d.
p-Xylene, m-xylene	0.094	0.084	< loq	< loq	< loq	< loq	n.d.	n.d.
1.1.2.2-tetrachloroethane	0.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Isopropilbenzene	0.14	0.14	< loq	n.d.	n.d.	0.024	< loq	< loq
Sec-butylbenzene	0.19	n.d.	n.d.	n.d.	n.d.	n.d.	< loq	n.d.
Phenol	n.d.	n.d.	0.23	n.d.	n.d.	< loq	< loq	n.d.
1.3.5-trimethylbenzene	n.d.	n.d.	n.d.	< loq	0.034	n.d.	n.d.	n.d.
p-Isopropilbenzene	0.19	0.18	0.033	0.053	0.062	< loq	0.015	0.063
D-limonene	0.20	0.20	0.084	0.083	0.13	< loq	0.106	0.14
Butylbenzene	n.d.	n.d.	n.d.	n.d.	n.d.	< loq	n.d.	n.d.
Naphthalene	0.104	n.d.	n.d.	0.044	n.d.	0.028	0.033	n.d.
Citral	0.33	n.d.	0.22	0.19	n.d.	n.d.	n.d.	n.d.
Counmarin	n.d.	n.d.	n.d.	n.d.	n.d.	1.44	< loq	6.1[a]
Geraniol	0.23	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cinnamyl alcohol	2.5	0.39	< loq	1.5	n.d.	n.d.	n.d.	n.d.
Isoeugenol	0.46	n.d.	0.143	0.73	n.d.	n.d.	n.d.	n.d.
Tributyl phosphate	0.49	n.d.	n.d.	n.d.	n.d.	0.13	0.017	< loq

n.d. (not detected) lower than the limit of detection.

[a] Concentration out of the linear range.

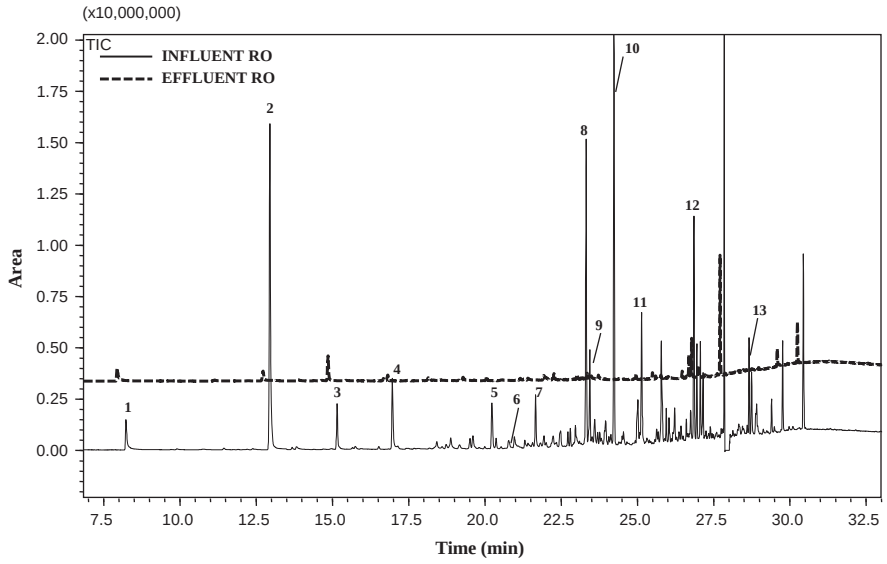

Fig. 3. GC chromatograms of influent and effluent samples belonging to the waste water treatment plant. Peak numbers refer to (1) 1,2-dichloroethane, (2) 1,1,2-trichloroethane, (3) ethylbenzene, (4) isopropilbenzene, (5) sec-butylbenzene, (6) p-isopropilbenzene, (7) D-limonene, (8) naphthalene, (9) citral, (10) geraniol, (11) cinnamyl alcohol, (12) isoeugenol and (13) tributyl phosphate.

units of seawater. This organophosphorus compound is used as a solvent in inks, synthetic resins, gums, adhesives and herbicide and fungicide concentrates.

As a general trend, it was observed that the majority of the micropollutants were reduced by using reverse osmosis membrane treatments.

4. Conclusions

In this present study, headspace solid phase microextraction with a PDMS/DVB fibre combined with gas chromatography–mass spectrometry was used to determine 76 micropollutants in water including volatile organic compounds as described in the introduction, endocrine disrupting compounds, odour compounds, fragrance allergens and some pesticides.

The method developed is sensible, shows good linear range, reproducibility, repeatability and low detection limits (at low ng L^{-1} levels). The validated method has been used for the determination of the target organic micropollutants in aqueous samples belonging different water treatment of application research units. The optimized method showed good performance in the different types of waters studied. The results indicated that the proposed method could be used to analyze the 76 micropollutants in water samples.

Some micropollutants were found in the samples, due to the fact that these species are commonly used in domestic and industrial applications. The tendency of most of them indicates a possible removal by the membrane reverse osmosis treatment. A cost-effective screening technique was developed to allow the study of removal of priority compounds by membrane systems, which does not use solvent and allows characterization of a large variety of compounds simultaneously.

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