Suitability of polypropylene microporous membranes for liquid- and solid-phase extraction of halogenated anisoles from water samples

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Abstract

The applicability of disposable polypropylene microporous membranes (MMs) for the concentration of five halogenated anisoles in water samples was investigated. Two microextraction approaches, named MM solid-phase extraction (MMSPE) and liquid-liquid extraction (MMLLE), are proposed. They are based on adsorption of target species onto the surface of the dry membrane and absorption into a few microlitres of solvent embedded in the pores of the membrane, respectively. The effect of several factors, such as sampling mode, type of acceptor solvent, ionic strength of the sample, stirring, sampling time, etc., on the performance of both approaches was thoroughly assessed. After extraction, analytes were recovered from the sorbent using just 0.25 mL of n-hexane and determined by gas chromatography with micro-electron-capture detection (GC-micro-ECD). Under optimised conditions, similar precisions (RSDs from 7 to 14%, under reproducibility conditions) and limits of quantification (values between 0.3 and 15 ng L^{-1}), as well as remarkable linear responses were attained for both techniques; however, MMSPE, operating in the headspace sampling mode (HS), showed faster kinetics for all species, was less affected by the type of matrix and the set-up of the extraction step was simpler, since immobilisation of the extraction solvent in the membrane was not necessary. Obtained results demonstrated, for the first time, the suitability of polypropylene MMs as adsorbents of lipophilic compounds.

Keywords: polypropylene microporous membranes; microextraction techniques; halogenated anisoles; gas chromatography.

1. Introduction

The determination of halogenated anisoles in aqueous matrices is an issue of concern due to their unpleasant taste and flavour, noticeable at extremely low concentration levels, ca. ng L^{-1} range [1-3]. Their presence in water samples has been related to the use of chlorine-based disinfectants and the existence of humic acids in water sources. The oxidative degradation of the latter compounds leads to the formation of halogenated phenols, which might undergo a further bio-methylation reaction to generate the corresponding halogenated anisoles with strong off-flavour properties [4-5].

From an analytical perspective, the determination of halogenated anisoles in water samples at the very low ng L^{-1} level relies on the use of gas chromatography either with electron-capture detection (GC-ECD), or combined with mass spectrometry (GC-MS), after an effective enrichment process [1,6-7]. In fact, efficiency and selectivity of the sample preparation step are crucial factors controlling the performance of the whole analytical procedure. Solid-phase extraction, closed-loop stripping and pervaporation have been proposed as valuable sample preparation approaches for the GC determination of haloanisoles [8-10]. Solid-phase microextraction (SPME) [1,3,6,11] and other related techniques, such as stir bar sorptive extraction (SBSE) [2,12] and headspace sorptive extraction (HSSE) [7] constitute a further improvement in the development of sample preparation methodologies for the determination of anisoles. Miniaturization, reduction in the consumption of organic solvents and high enrichment factors are their major advantages. However, on the other hand, SPME and SBSE are prone to carry-over effects and sorbents (coated fibres and stir bars) are still expensive and also, case of SPME fibres, relatively fragile.

The above drawbacks can be overcome considering liquid-phase microextraction (LPME) as alternative to SPME and SBSE [13]. LPME processes can be carried out in different configurations. The simplest one, named as single-drop microextraction (SDME), uses a few microlitres (typically 1-3 μL) of a suitable solvent maintained at the tip of a microsyringe needle [13-17]. Although it provides high extraction factors, the solvent drop can be easily dislodged, particularly if samples are stirred vigorously and/or long sampling periods are considered. Immobilisation of the extraction solvent (acceptor phase) in a porous membrane avoids the aforementioned problem, and thus, it constitutes a much more robust format for LPME. In practise, polypropylene microporous membranes (MMs), in a hollow-fibre (HF) configuration, are the preferred media to support the acceptor phase, which can be contained in both, the lumen and the pores of the fibre [18-23], or just in the pores [24]. In this latter modality, immobilisation of the liquid-phase in the MM is simpler and faster than in the former one [24]. Extractions using a few microlitres of solvent loaded in a hollow MM have been termed as hollow-fibre liquid-phase microextraction (HF-LPME) [20,22-23], hollow-fibre microporous membrane liquid-liquid extraction (HF-MMLLE) [13,18], or just microporous membrane liquid-liquid extraction (MMLLE) [24]. As far as we know, the applicability of LPME for the extraction and concentration of halogenated anisoles from aqueous matrices has been evaluated only in the SDME format.

In this research, hydrophobic HF polypropylene MMs have been evaluated for the extraction and concentration of five halogenated anisoles from water samples. Two sets of extraction conditions, based on adsorption and absorption mechanisms, are proposed. In the first case, the porous membrane is used directly as solid-sorbent to extract target species. In the second mode, pores were previously loaded with a few microliters of an organic solvent. The effects of several variables, such as the sampling mode, exposure time, ionic strength, stirring, etc. on the performance of the sample preparation, using solid or liquid-phase microextraction processes, are discussed. Whatever the extraction mechanism, analytes were recovered from the MM using 0.25 mL of an appropriate solvent and determined by gas chromatography with micro-electron-capture detection (GC-micro-ECD).

2. Experimental

2.1. Chemicals and material

Trace analysis quality solvents: acetone, n-hexane, toluene and n-nonane, as well as sodium chloride were acquired from Merck (Darmstadt, Germany). Standards of 2,4-dichloroanisole (DCA), 2,4,6-trichloroanisole (TCA), 2,4,6-tribromoanisole (TBA), 2,3,4,6-tetrachloroanisole (TeCA) and pentachloroanisole (PCA) were purchased from Aldrich (Milwaukee, WI, USA) and Supelco (Bellefonte, PA, USA). The internal standard (I.S.), 4-iodoanisole (IA), was supplied by Aldrich. Individual solutions of each anisole were made in acetone, further dilutions and mixtures of them were prepared in the same solvent. The stock solution of IA was prepared in acetone and then diluted with n-nonane.

Accurel polypropylene Q3/2 membranes in a HF configuration (600 µm I.D., 200 µm wall thickness, 0.2 µm pore size) were purchased from Membrana (Wuppertal, Germany) in bundles consisting of hundreds of fibres with a length of 0.6 m. They were cut in pieces with a length of 2 cm, using a sharp blade, soaked with acetone for 30 min, allowed to dry and stored in a closed vessel. The cost per extraction unit (2 cm HF membrane) remained below 0.05 Euro, thus, membranes were considered as single-use devices.

2.2. Sample preparation

Performance of the microextraction approaches investigated in this work was assessed with spiked and non-spiked samples of ultrapure (Milli-Q), river and wastewater. In the latter case, grab samples were taken in the inlet and outlet streams from an urban sewage plant equipped with primary and secondary (activated sludge) treatments. River and wastewater samples were passed through glass fibre filters before addition of target species. Extractions were accomplished in 120 mL glass vessels furnished with PTFE-lined septa and aluminium caps (Sugelabor, Madrid, Spain). A stainless steel wire (0.6 mm diameter), acquired from a local hardware store, was inserted through the septum of the extraction vessel and along the lumen of the HF. Thus, only the outlet surface and the pores in the walls of the polypropylene MM, but not the lumen, were available to analytes. The length of the wire connecting the HF with the septum of the sampling vessel was adjusted to 2 or 6 cm, depending on the considered sampling mode.

As regards the extraction step, two sets of experimental conditions were investigated. In one case, anisoles were adsorbed onto the surface of the MM, which did not contain any organic solvent. Under final working conditions, the membrane was placed at the headspace (HS) of a vessel containing 80 mL of water with a 30% of sodium chloride. This approach is referred as headspace microporous membrane solid-phase extraction (HS-MMSPE). The sampling step was adjusted to 2 hours and no stirring was used. In the second mode, the membrane, with the stainless steel wire along its lumen, was first immersed in a suitable organic solvent for 5 min. Assuming that pores represent around 66% of the volume of the membrane [24], 6.5 µL of solvent (n-nonane under optimised conditions) were immobilised in the fibre. After that, it was dipped in the sampling vessel containing 115 mL of water. No salt was added and the exposure period was increased to 4 hours. Samples were stirred (500 rpm) using a PTFE-coated stir bar (20 x 5 mm) to increase the mass transference kinetics. Following the same criteria as Zorita et al. [24], this extraction alternative was termed MMLLE.

In both approaches, after finishing the extraction step, sampling vessels were opened and the stainless steel wire, connecting the membrane and the septum, held with tweezers and cut using pliers. The membrane, still attached to about 5 mm of wire, was transferred to a 0.3 mL insert in a 1.5 mL GC vial. Then, 250 µL of n-hexane were added, the vial was crimped and analytes were extracted for 5 min at room temperature. After removing the extraction assembly, 50 µL of a

solution of IA in n-nonane (with a concentration between 50 and 500 ng mL^{-1}) were added and the extract was concentrated to ca. 50 µL using a gentle stream of nitrogen.

2.3. Instrumentation

An Agilent 6890 gas chromatograph (Wilmington, DE, USA) furnished with a split/splitless injection port and a micro-electron-capture detector (micro-ECD) was employed to measure the concentration of target compounds in the final extracts from water samples. Analytes were separated with an Agilent HP-5 type capillary column (30 m x 0.25 mm I.D., d_f: 0.25 µm) operated at a constant helium flow of 1.2 mL min^{-1}. The oven temperature was programmed as follows: 110 ºC (1 min), first rate at 5 ºC min^{-1} until 170 ºC, second rate at 12 ºC min^{-1} until 260 ºC (held for 5 min). Injector and detector temperatures were set at 270 and 300 ºC, respectively. Extracts (2µL volume) were injected in the splitless mode (purge time 1 min) using an autosampler. The makeup nitrogen flow in the micro-ECD system was fixed at 60 mL min^{-1}.

3. Results and discussion

3.1. Extraction mechanism and sampling mode

Up to now, polypropylene MMs have always been considered as inert supports of the acceptor phase in LPME processes. Although the group of Popp [25] had already suggested that the porous polypropylene membrane, itself, could contribute to the extraction of compounds with high octanol-water partition coefficients (K_{ow}) from water samples, this possibility was not further explored in the literature. On the other hand, porous polypropylene coated with different polymers has been employed for solid-phase extraction of low [26] and medium polarity compounds [27-28]. Surprisingly, in these works data regarding the adsorption capability of the hydrophobic template are not provided.

To investigate the contribution of the sampling mode (direct vs. HS) and the retention mechanism (adsorption vs. absorption) to the extraction of haloanisoles from water samples, using HF polypropylene MMs, two series of experiments were carried out. In one case, the membrane was maintained at the HS of the vessel, which contained 80 mL of sample. The second series of extractions was accomplished dipping it in the sample (115 mL), which filled nearly completely the extraction vessel. Aliquots of the same spiked water sample (1 ng mL^{-1} for DCA and 0.1 ng mL^{-1} for the rest of species) were used in all experiments. The exposure period was adjusted to 3 hours and samples were stirred using a PTFE coated bar. Triplicate extractions with dry membranes and impregnated with toluene or n-nonane were done. The choice of these two solvents as acceptor phase was made considering their compatibility with the hydrophobic polypropylene membrane [16, 29-33] and affinity for target species.

After finishing the extraction period analytes were recovered with 0.25 mL of n-hexane and extracts concentrated to approximately 50 µL, as described in the experimental section. The efficiency of the desorption step ranged from 90 to 92%, and it did not increase when contact times longer than 5 min were considered. As membranes were employed as disposable devices, the above desorption yields were considered acceptable to proceed with the optimisation of the method. Ratios between peak areas for target analytes and the I.S. remained unmodified after reduction of the extracts from 250 to 50 µL, which indicated the absence of significant losses during the evaporative concentration step, data not shown.

Fig. 1 plots the responses (corrected peak areas) obtained in both series of experiments. Operating in the direct sampling mode (Fig. 1A) the highest extraction efficiencies corresponded to membranes impregnated with n-nonane,

whereas little differences were noticed between responses attained for dry membranes and those with toluene embedded in the pores. In the HS mode (Fig. 1B), dry membranes clearly provided the highest responses for TeCA, TBA and PCA (log K_{ow} 4.5, 4.2 and 5.0, respectively). For the more polar TCA and DCA (log K_{ow} 3.9 and 3.4, respectively), the achieved values were similar or just slightly lower than those corresponding to membranes impregnated with n-nonane. Globally, these results pointed out that adsorption of haloanisoles in polypropylene MMs is a process of utmost importance, particularly for the most lipophilic compounds. It also seems that the adsorption mechanism is more favourable when analytes have been previously volatilised from the sample. Probably, the internal surface of the pores in the hydrophobic membrane is not available to the water sample; therefore, in the direct sampling mode, analytes are just adsorbed onto the outlet surface of the porous membrane. On the other hand, this limitation is overcome in the HS mode.

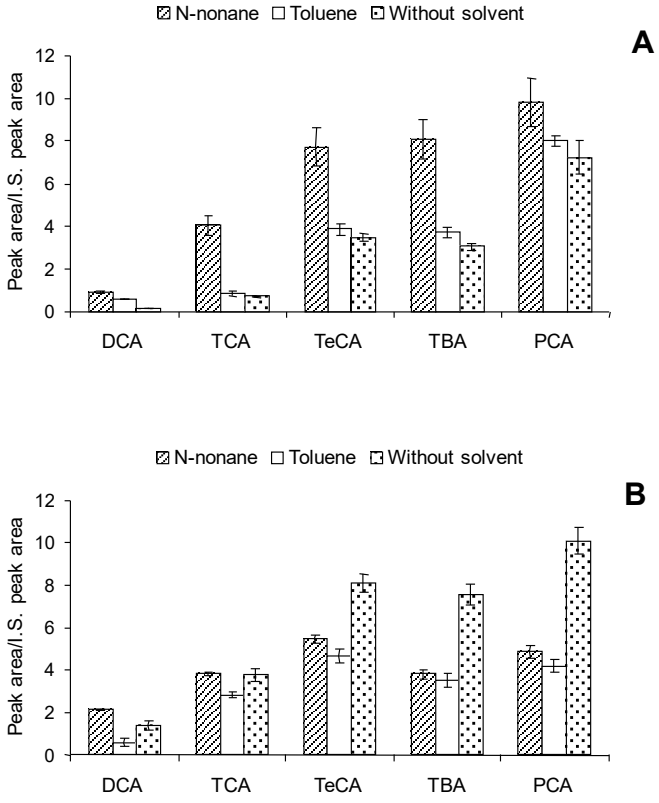


Fig. 1. Responses obtained as function of the sampling mode and extraction solvent. A, Direct sampling. B, HS extraction. N=3 replicates.

3.2. Optimisation of extraction conditions

On the basis of the above data, it was decided to carry out a thorough optimisation of those factors affecting the performance of the extraction under the most favourable conditions: (1) direct sampling using membranes impregnated with n-nonane, referred as MMLLE and (2) HS extraction with dry membranes, named as HS-MMSPE. In both cases, extractions were performed at room temperature, considering samples spiked in the range from 0.02 to 0.5 ng mL^{-1} (10 times higher values were used for DCA) and an exposure period of 4 hours.

3.2.1. MMLLE conditions

In order to avoid losses of the analytes due to partition in the HS, MMLLE experiments were carried out using vessels filled nearly completely with spiked water samples (115 mL). As a first step in the optimisation of MMLLE conditions, membranes were immersed in n-nonane for different times (5 to 30 min) before being exposed to the spiked samples. This variable showed a negligible effect on the efficiency of the further extraction. Thus, it was fixed to 5 min for the rest of the study.

Fig. 2 compares the responses for stirred (500 rpm) and non-stirred samples. As expected, stirring speeded up the diffusion of the halogenated anisoles from the bulk of the water sample to the interface with the sorbent, improving the yield of the microextraction process. Stirring rates higher than 500 rpm were not considered since they induced the presence of air bubbles around the porous membrane reducing the surface of contact with the sample. As regards the effect of the ionic strength on the efficiency of the MMLLE, for DCA and TCA, the most polar of the considered analytes, the yield of the extraction remained unchanged for NaCl concentrations up to 15%, whereas for the rest of species it decreased slightly for salt concentrations over 5%, probably due to the increase in the viscosity of the sample, which affected negatively the extraction kinetics, data not shown. This behaviour matched with results obtained for LPME of PAHs and phthalates, using toluene immobilised in polypropylene microporous fibres [24, 29]. NaCl concentrations over 15% led to the formation of a precipitate in the surface of the HF membrane that worsened the precision of the extraction, data not shown. Based on these results, salt addition was not considered in further MMLLE experiments.

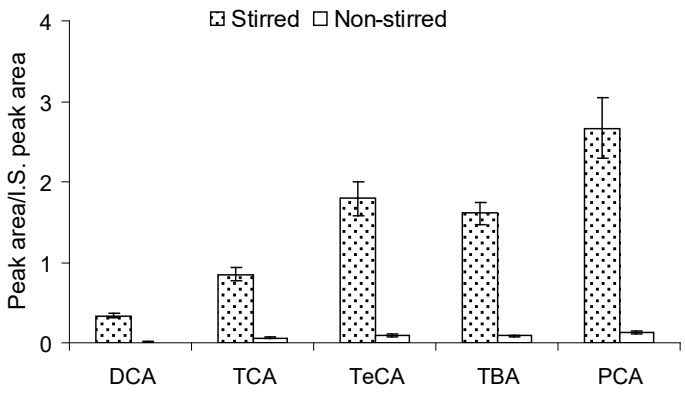


Fig. 2. Effect of stirring on the performance of MMLLE using n-nonane as acceptor solvent. N=3 replicates.

Adding a small volume of a miscible organic solvent to water samples has been reported as favourable to improve the efficiency and precision in the microextraction of haloanisoles, since it minimizes analytes losses due to adsorption in the walls of glass vessels [2]. In practise, the addition of a 5% of acetone (6 mL) to water samples resulted in a moderate reduction (around 20%) in the efficiency of the extraction.

3.2.2. HS-MMSPE conditions

It is well known that the ratio between sample and HS volumes plays a significant effect on the efficiency of solid-phase microextractions [35]. Using 120 mL vessels, the amount of anisoles adsorbed on MM increased with the volume of water

sample between 20 and 80 mL (higher volumes could not be tested since they are incompatible with the HS sampling mode) Table 1. Additional assays, employing a fixed amount of water and variable HS volumes (this was achieved introducing a given amount of glass beads in the extraction vessel), proved that the latter factor has a negligible effect on the extraction process, data not given. This behaviour indicates a high extraction capability for the polypropylene MM sorbent, probably related to its high specific surface: 24 $m^2 g^{-1}$ [36].

	Water volume (mL)			
Analyte	20	40	60	80
DCA	38%	59%	79%	100%
TCA	36%	60%	81%	100%
TeCA	36%	60%	84%	100%
TBA	36%	58%	81%	100%
PCA	33%	56%	82%	100%

Table 1. HS-MMSPE normalised responses for different sample volumes. Average values for duplicate experiments.

Conversely to results obtained for MMLLE, stirring did not affect the efficiency of the HS-MMSPE process, therefore, no stirring was applied in further experiments. The effect of the ionic strength is shown in Fig. 3. The depicted trend is different to that reported for MMLLE and concordant with the behaviour reported for HSSE [7] and HS-SPME of anisoles [6] using polydimethylsiloxane sorbents: the efficiency of the extraction increased steady with the concentration of sodium chloride added to the sample between 0 and 30%.

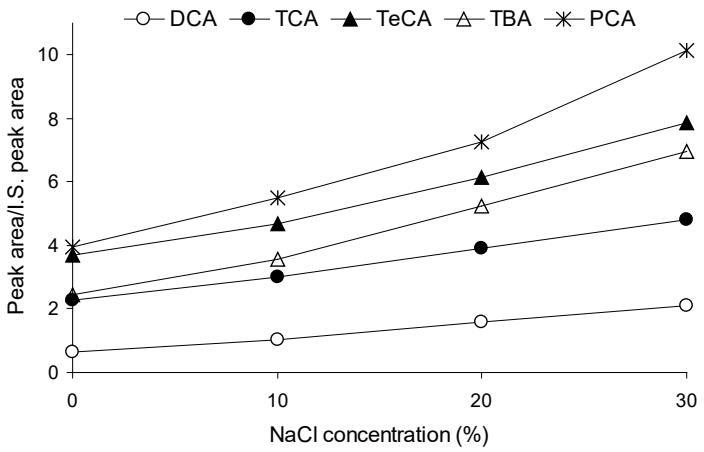


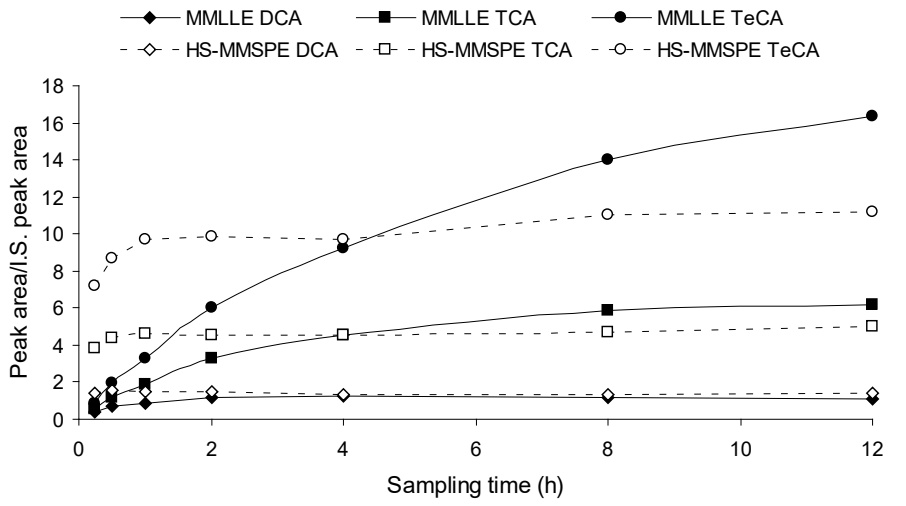
Fig. 3. Efficiency of HS-MMSPE as function of the ionic strength. Average data for duplicate extractions.

As in the case of MMLLE, the addition of a 5% of acetone to the samples reduced the efficiency of the extraction; however, in this case a dramatic diminution (between 70 and 80% depending on the compound) was noticed, data not shown. This negative effect can be explained by two contributions: (1) an increase in the solubility of the analytes and (2)

competence between acetone and anisoles by the available surface of the polypropylene membrane, which is a relevant phenomena in adsorption based extractions.

3.3. Extraction kinetics

Time-course of MMLLE and HS-MMSPE processes, under conditions optimised in the previous section, are shown in Fig. 4. Depicted data correspond to aliquots of the same ultrapure water sample spiked at 50 ng L^{-1} (500 ng L^{-1} for DCA). As observed, kinetics of mass transference from the sample to the MM was much faster for HS-MMSPE than for MMLLE. For the first technique, all compounds reached the equilibrium after an exposure period of 2 hours, whereas in the latter approach only DCA and TCA achieved the equilibrium within the considered interval of time. On view of data plotted in Fig. 4, HS-MMSPE clearly provides higher responses than MMLLE when extraction times under 2 hours are considered. Taking into account the kinetics of both processes, and the need of maintaining a high sample throughput, 2 and 4 hours were adopted as sampling times in further experiments performed with HS-MMSPE and MMLLE, respectively. Obviously, this implies that in the first situation extractions are carried out under equilibrium conditions, whereas the kinetics region is used in the second one.



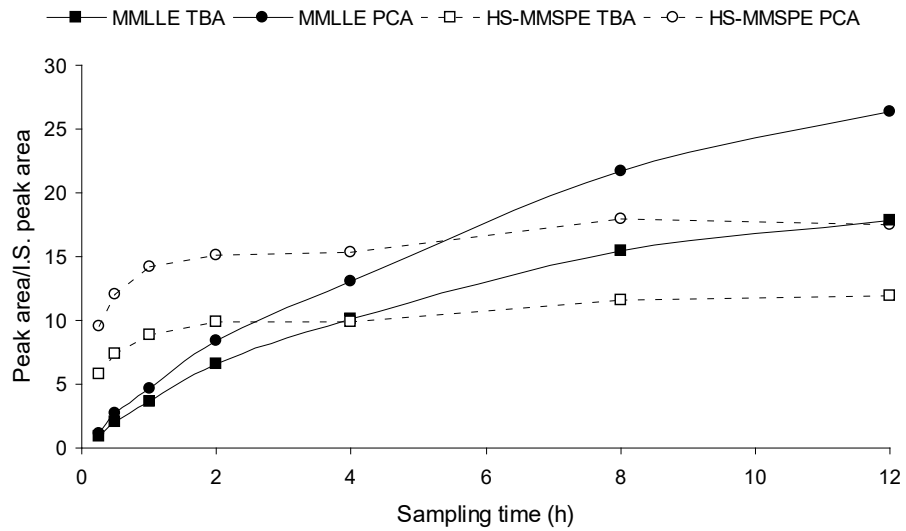


Fig. 4. Time-course of MMLLE and HS-MMSPE under final working conditions.

3.4. Performance evaluation

Table 2 summarizes some data related to the precision of both approaches for samples spiked at different concentration levels. Repeatability of HS-MMSPE, given as relative standard deviations (RSDs) for samples extracted the same day, remained below 8%. RSDs for extractions carried out in different days ranged from 10 to 13%. In general, MMLLE showed a slightly better precision than HS-MMSPE, except for samples spiked at 10 ng L^{-1}, for which RSDs between 9 and 14% were observed. Globally, these RSD values are similar to those reported for SBSE [2], HSSE [7], SPME [1, 6] and SDME [14] for samples fortified at similar concentrations.

	HS-MMSPE				MMLLE			
	Intra-day			Inter-day	Intra-day			Inter-day
Added conc.	5 ng L^{-1}	25 ng L^{-1}	100 ng L^{-1}	25 ng L^{-1}	10 ng L^{-1}	25 ng L^{-1}	100 ng L^{-1}	25 ng L^{-1}
DCA[a]	5.9	7.4	7.5	11.2	13.8	2.4	2.4	9.2
TCA	5.5	6.8	5.4	11.6	8.6	2.5	1.8	10.8
TeCA	4.3	6.6	4.7	11.9	11.9	2.3	1.5	7.6
TBA	7.7	8.1	7.6	12.5	11.7	1.5	1.8	9.4
PCA	2.8	7.1	3.0	10.4	12.7	1.1	1.4	11.3

Table 2. Intra-day (n=4 replicates) and inter-day (n=9 replicates in 3 different days) precision of both extraction techniques for samples spiked at different concentration levels. Relative standard deviations (RSDs) given as percentages. [a] DCA spiked concentrations were 10 times higher

Linearity was evaluated with samples spiked at increased concentrations between 2.5 and 500 ng L^{-1} (25 to 2500 ng L^{-1} for DCA). Correlation coefficients for the corresponding calibration graphs ranged from 0.997 to 0.999 for both extraction techniques, Table 3. Extraction efficiencies (EEs) were assessed as the ratio between responses for each compound in the extracts obtained from spiked water samples (addition level 50 ng L^{-1}) and those corresponding to the addition standard. In general, the HS-MMSPE method provided slightly higher yields (from 24% to 52%) than MMLLE (from 16% to 42%). Enrichment factors (EFs), calculated using above extraction yields and the ratio between sample (80 and 115 mL for HS-MMSPE and MMLLE, respectively) and final extract volumes (0.05 mL), ranged from 300 to 1000 times, depending on the considered compound, Table 3. As regards the achieved limits of quantification (LOQs), defined for a signal to noise (S/N) ratio of 10, values equal or below 0.5 ng L^{-1} were achieved for TeCA, TBA and PCA with both extraction approaches. For DCA and TCA, slightly lower LOQs were attained with HS-MMSPE than using MMLLE. The reason for such differences was the better selectivity of the HS sampling mode, which led to a lower baseline noise, particularly in the first half of the GC-ECD chromatogram.

HS-MMSPE	MMLLE

	Correlation coefficient (R^2)	EE (%)	EF	LOQ (ng L^{-1})	Correlation coefficient (R^2)	EE (%)	EF	LOQ (ng L^{-1})
DCA	0.9974	24 ± 2	387	10	0.9987	16 ± 1	374	15
TCA	0.9994	40 ± 2	646	1	0.9992	33 ± 3	769	1.5
TeCA	0.9993	48 ± 3	761	0.5	0.9990	40 ± 2	911	0.4
TBA	0.9990	39 ± 3	629	0.5	0.9994	38 ± 4	871	0.4
PCA	0.9992	52 ± 4	833	0.4	0.9992	42 ± 3	967	0.3

Table 3. Linearity, extraction efficiencies (EE), enrichment factors (EF) and limits of quantification (S/N 10) for both microextraction methodologies.

3.5. Real samples analysis and matrix effects

The two extraction approaches optimised in this work were applied to river and sewage water. Samples were first filtered and then divided in two fractions. One was analysed directly and the other spiked with target species at 20 ng L^{-1}. Each fraction was processed in triplicate. None of the analytes was detected in the non-spiked fractions of tested samples, Fig. 5.

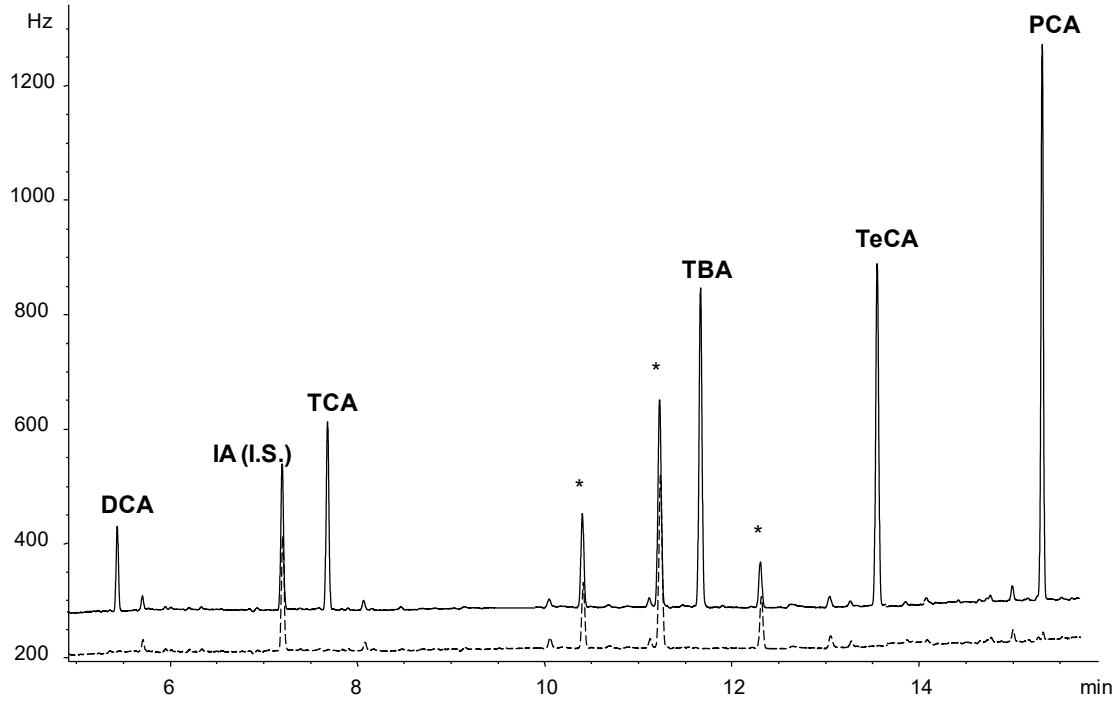


Fig. 5. GC-ECD chromatograms for non-spiked (dotted line) and spiked fractions (solid line) of a raw wastewater sample. HS-MMSPE. Addition level 20 ng L^{-1} (200 ng L^{-1} for DCA).* unidentified species.

Responses obtained for spiked fractions were compared with those measured for ultrapure water with the same addition level. Data, as relative recoveries, are summarized in Table 4. Using HS-MMSPE, no matrix effects were noticed for river and treated wastewater. For raw wastewater, the efficiency of the extraction underwent a reduction around 20% for TBA and PCA and remained unaltered for the other 3 species. With MMLLE, a moderate diminution in the yield of the extraction was

already noticed in treated wastewater for TeCA, TBA and PCA and it affected to all species in raw wastewater. Considering these results, external calibration can be applied to calculate the concentration of target anisoles in river and treated wastewater using HS-MMSPE as sample preparation technique, whereas the standard addition mode is recommended for raw wastewater. If MMLLE is the chosen extraction approach, external calibration is valid only for river water.

	HS-MMSPE			MMLLE		
Analyte	River water	Treated wastewater	Raw wastewater	River water	Treated wastewater	Raw wastewater
DCA[a]	101 ± 4	104 ± 4	107 ± 7	92 ± 9	100 ± 3	79 ± 7
TCA	101 ± 6	100 ± 4	100 ± 6	92 ± 12	92 ± 9	75 ± 5
TeCA	102 ± 3	102 ± 3	93 ± 6	90 ± 13	76 ± 13	63 ± 8
TBA	104 ± 9	107 ± 7	84 ± 7	95 ± 13	78 ± 12	61 ± 6
PCA	100 ± 10	105 ± 9	73 ± 9	91 ± 14	73 ± 13	44 ± 7

Table 4. Relative recoveries, with their standard deviations (n=4 replicates), for different water samples spiked at the 20 ng L^{-1}. [a]added concentration 200 ng L^{-1}.

4. Conclusions

Two microextraction approaches, based on the use of polypropylene MMs and named MMLLE and HS-MMSPE, have been proposed for the determination of five halogenated anisoles in water samples. Under optimised conditions, both techniques provided limits of quantification in the low ng L^{-1} range, acceptable precisions and linearity, therefore, they constitute interesting alternatives to other microextraction methods proposed for the concentration of halogenated anisoles in water samples, with the additional advantages of their low cost and no carry-over problems. From the point of view of the experimental set-up, HS-MMSPE was simpler than MMLLE, since (1) it avoided completely the use of organic solvents during extraction, and thus the previous step to impregnate the membrane with the acceptor phase (2) stirring was not necessary and (3) kinetics of extraction was faster than for MMLLE. Moreover, HS-MMSPE was less prone to matrix effects than MMLLE. On the other hand, it is expected that MMLLE might provide lower LOQs for TeCA, TBA and PCA when long sampling periods are employed.

From the best of our knowledge, this work constitutes the first application of polypropylene MMs as solid adsorbents in microextraction processes. On the basis of obtained results, it is expected that the MMSPE approach, operating in direct or HS sampling modes, will be of usefulness for the concentration of medium and low polarity organic compounds in water samples.

Acknowledgements

Financial support from Xunta de Galicia and EU FEDER funds (project PGIDIT06PXIB237039PR) is acknowledged. R. M. acknowledges a FPU grant from the Spanish Ministry of Education.

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