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Evaluation of polyethersulfone performance for the microextraction of polar chlorinated herbicides from environmental water samples

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ABSTRACT

In this work, the suitability of bulk polyethersulfone (PES) for sorptive microextraction of eight polar, chlorinated phenoxy acids and dicamba from environmental water samples is assessed and the analytical features of the optimized method are compared to those reported for other microextraction techniques. Under optimized conditions, extractions were performed with samples (18 mL) adjusted at pH 2 and containing a 30% (w/v) of sodium chloride, using a tubular PES sorbent (1 cm length × 0.7 mm o.d., sorbent volume 8 μL). Equilibrium conditions were achieved after 3 h of direct sampling, with absolute extraction efficiencies ranging from 39 to 66%, depending on the compound. Analytes were recovered soaking the polymer with 0.1 mL of ethyl acetate, derivatized and determined by gas chromatography–mass spectrometry (GC–MS). Achieved quantification limits (LOQs) varied between 0.005 and 0.073 ng mL^{-1}. After normalization with the internal surrogate (IS), the efficiency of the extraction was only moderately affected by the particular characteristics of different water samples (surface and sewage water); thus, pseudo-external calibration, using spiked ultrapure water solutions, can be used as quantification technique. The reduced cost of the PES polymer allowed considering it as a disposable sorbent, avoiding variations in the performance of the extraction due to cross-contamination problems and/or surface modification with usage.

1. Introduction

Chlorinated phenoxy acids constitute an important family of pesticides used to remove broad-leaved weeds from crops and gardens [1,2]. They are polar herbicides existing as negatively charged species at neutral pHs; thus, they can be easily released from application areas, e.g. by run-off waters, ending in surface water bodies and even polluting underground aquifers [3,4]. Chlorophenoxy acids, impurities contained in technical formulations [5], and their environmental degradation products [6,7] display a high toxicity to water organisms and are suspected to cause gastrointestinal effects and multi organ dysfunctions [8].

Liquid chromatography–tandem mass spectrometry (LC–MS/MS) [9,10] and gas chromatography (GC) followed by MS [11] are the preferred techniques for the determination of acidic herbicides in environmental and food samples. In case of GC–MS methods, a derivatization step is required to reduce the polarity of phenoxy acids and to enhance their thermal stability during injection and ionization [11–13]. Due to their high water solubility, the extraction and concentration of phenoxy acids from water samples remain challenging issues. One the most resorted approaches is solid-phase extraction (SPE), normally relying on graphitized carbon materials [14,15] or polymeric sorbents [16]. Other options involve microextraction techniques. As regards solid-phase modalities, in-tube solid-phase microextraction (*in-tube* SPME) was coupled with LC–MS/MS for the automated and sensitive determination of phenoxy acids in surface water samples. A key factor which controlled the efficiency of the process was the coating of the capillary column, with the highest extraction yield corresponding to polar polyethylene glycol phases [17]. SPME, followed by *on-fibre* derivatization and GC–MS, has been also proposed for the determination of phenoxy acids in environmental water samples. Again, the best performance was provided by polar polyacrylate (PA) SPME fibres [18,19] with limits of quantification (LOQs) below 0.1 ng mL^{-1}. Other authors have proposed the in-situ derivatization of acidic herbicides, with alkyl choroformates and benzyl halides, to decrease their polarity and, thus, to improve their affinity to less polar SPME coatings [20,21]. However, for

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complex samples, in-situ derivatization often lacks in quantitative and reproducible yields. Stir-bar sorptive extraction (SBSE), with polydimethylsiloxane (PDMS) coated *Twisters*^{TM}, followed by solvent desorption, post-extraction derivatization and GC–MS determination has attained LOQs from 0.06 to 1.2 ng mL^{-1}, considering injection volumes up to 20 μL [22]. Independently of their extraction efficiencies, above microextraction techniques share two drawbacks: (1) the limited stability of sorbent devices under sampling conditions (extractions are usually carried out exposing fibres and coated stir bars directly to samples adjusted at pH 2–3), leading to variations in the extraction efficiency with the aging of the sorbent, and (2) the risk of cross-contamination problems, derived from the use of the same device for different samples.

Liquid-phase microextraction (LPME) overcomes the above shortcomings since a fresh acceptor solution is employed for each extraction. In this context, cloud-point microextraction [23], with toluene as acceptor phase and a quaternary ammonium salt as ion-pair formation agent, and dynamic hollow fibre (HF) LPME [4], using a disposable polypropylene porous membrane impregnated with toluene, have been successfully applied to the extraction of phenoxy acids from aqueous samples.

In addition to main trends in solid- and liquid-phase microextraction, the use of disposable devices has been also reported for sorptive extraction of trace organic compounds. Usually, analytes are concentrated in technical grade, low cost, bulk sorbents from where they are further recovered either using a suitable solvent, or considering thermal desorption. Disposable sorbents combine the operational simplicity of SPME and SBSE with the feasibility of simultaneously processing several samples, increasing the productivity of the method, and avoiding variations in the efficiency of the extraction process due to partial losses of the coating material, chemical modification and/or surface contamination [24]. In a recent study, the suitability of different materials for solid-phase microextraction of a large family of pollutants from water samples was compared [25]. Polyethersulfone (PES) emerged as the best choice for polar species, improving significantly the extraction efficiencies provided by silicone and polypropylene polymers. These earlier results have been confirmed with further applications focused on different families of polar chemicals [26,27].

Within the above context, the aim of this study was to evaluate, for first time, the capabilities of PES for the extraction and concentration of eight polar phenoxy acids and dicamba, as underivatized species, from environmental water samples. Parameters affecting the performance of the extraction process have been systematically investigated, including a direct comparison between the efficiency of this polymer and that provided by *Twisters* coated with a 3-fold higher amount of sorbent. Analytes were recovered from the PES sorbent using just 0.1 mL of ethyl acetate. After a single step derivatization process, they were quantified by GC–MS.

2. Experimental

2.1. Standards, solvents and sorbents

Standards of phenoxy acid herbicides and dicamba were obtained from Sigma-Aldrich (Milwaukee, WI, USA); 2,4-dichlorophenoxy-d_3-acetic-2,2-d_2 acid (2,4-D-d_5), used as internal surrogate (IS) throughout the sample preparation process, was provided by CDN isotopes (Quebec, Canada). Full names, abbreviations and some relevant properties of target compounds are summarized in Table 1. Individual stock solutions of the above analytes and diluted mixtures, used to spike water samples employed during optimization of extraction conditions, were prepared in acetonitrile and stored at 4 °C for a maximum of 2 months. A second set of individual standards and mixture solutions were prepared in ethyl acetate. Silylated derivatives of target compounds, and the internal surrogate (IS), were obtained by adding the derivatization reagent to standards in ethyl acetate.

Hydrochloric acid and sodium chloride (NaCl) were supplied by Merck (Darmstadt, Germany). Acetonitrile (HPLC grade) and ethyl acetate (trace analysis grade) were also purchased from Merck. The silylation reagent, *N*-methyl-*N*-(*tert*-butyldimethylsilyl) trifluoroacetamide (MTBSTFA), was provided by Sigma-Aldrich. Ultrapure water was obtained from a Milli-*Q* system (Millipore, Billerica, MA, USA).

The PES sorbent was acquired from Membrana (Wuppertal, Germany) in a tubular format (0.7 mm external diameter, 1.43 g mL^{-1} density). Pieces of this polymer (1 cm length) were cut and soaked twice with ethyl acetate for 15 min. Thereafter, they were dried with a lint-free tissue and kept in closed glass vessels until being used. Given their reduced cost (ca. 0.05 Euro/unit), sorbents were discarded after each use. PDMS coated stir-bars (*Twisters*, PDMS volume 24 μL), considered for comparative purposes, were provided by GERSTEL (Mülheim an der Ruhr, Germany). Nitrocellulose membrane filters (47 mm diameter, 0.45 μm pore size) were purchased from Millipore (Bedford, MA, USA).

2.2. Samples and sample preparation

Water samples involved in this study were obtained from creeks, flowing through agriculture areas, and from an urban sewage treatment plant (STP) located in the Northwest of Spain. Surface and sewage water samples were collected in glass vessels and transported immediately to the laboratory for filtration. Thereafter, they were stored at 4 °C, for a maximum of 2 days, before extraction.

Microextraction experiments were performed in glass vessels (20 and 120 mL volume recipients were considered) containing a PTFE covered stir bar and equipped with PTFE layered septa and aluminium crimp caps. The PES sorbent was dipped in the sample and allowed to turn freely during extraction. Thereafter, it was removed with tweezers, rinsed using ultrapure water and dried with a lint-free tissue. Analytes were desorbed by soaking the polymer with a suitable solvent. The organic extract was transferred to a second insert containing MTBSTFA as derivatization reagent. Under optimized conditions, 18 mL samples, previously adjusted at pH 2, were poured in 20 mL extraction vessels containing 5.4 g of NaCl (30% w/v). Extractions were carried out at room temperature in a multi-position magnetic plate using a stirring rate of 550 rpm for 3 h. Thereafter, the sorbent was soaked during 15 min with 0.1 mL of ethyl acetate. The organic extract was withdrawn and mixed with 10 μL of MTBSTFA, in order to transform native species in their silylated derivatives. After 45 min of reaction at room temperature, extracts were kept at −20 °C until injection in the GC–MS system.

2.3. Determination conditions

Compounds were determined using an Agilent (Wilmington, DE, USA) GC–MS system consisting of a 7890A gas chromatograph and a quadrupole mass analyzer (Agilent model 5975C), furnished with an electron ionization (EI) source. Derivatized herbicides were separated in a HP-5 MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) provided also by Agilent. Helium (99.999%) was used as carrier gas at a constant flow of 1.3 mL min^{-1}. Injections (2 μL) were made in the splitless mode (splitless time 1 min) with the injector port at 280 °C. The chromatographic oven was programmed as follows: 100 °C (1 min), 1st rate at 10 °C min^{-1} to 180 °C (1 min), 2nd rate at 3 °C min^{-1} to 200 °C, 3rd rate at 15 °C min^{-1} to

Table 1
Database of target herbicides with relevant physico-chemical properties, retention times and recorded ions for their silyl derivatives.

Compound	CAS number	Abbreviated name	p*Ka*	LogK_{ow}	Retention time (min)	Quantification ion (*m*/*z*)	Confirmation ions (*m*/*z*)
2-(4-Chloro-2-methylphenoxy) propanoic acid	93-65-2	Mecoprop	3.19	2.56	7.99	225	271, 129
3,6-Dichloro-2-methoxybenzoic acid	1918-00-9	Dicamba	2.40	2.57	8.19	277	262, 203
4-Chloro-2-methylphenoxy acetic acid	94-74-6	MCPA	3.14	2.21	8.56	257	229, 211
2-(2,4-Dichlorophenoxy) propanoic acid	120-36-5	2,4-DP	3.03	2.78	8.82	219	245, 291
2,4-Dichlorophenoxy acetic acid	94-75-7	2,4-D	2.98	2.43	9.51	277	213, 233
2-(2,4,6-Trichlorophenoxy) propanoic acid	93-72-1	2,4,5-TP	2.93	3.45	10.77	279	327, 253
2-(2,4,5-Trichlorophenoxy) acetic acid	93-76-5	2,4,5-T	2.88	3.10	11.66	311	283, 253
4-(4-Chloro-2-methyphenoxy) butanoic acid	94-81-5	MCPB	4.58	3.36	12.30	199	285, 201
4-(2,4-Dichlorophenoxy) butanoic acid	94-82-6	2,4-DB	4.56	3.39	13.53	219	305, 221
2,4-Dichlorophenoxy-d_3-acetic-2,2-d_2 acid	352438-69-8	2,4-D-d_5	–	–	9.44	282	238

Table 2
Experimental domain and standardized values for main effects and two-factor interactions obtained during optimization of microextraction conditions.

	Main effects			Two-factor interactions		
	pH (2–6)	NaCl (%) (10–30)	Stirring speed (rpm) (300–800)	pH-NaCl	pH-stirring speed	NaCl-stirring speed
Mecoprop	−2.69*	2.28	−0.03	−1.7	0.1	−0.1
Dicamba	−7.92*	4.56*	0.71	−3.1*	−0.9	−0.5
MCPA	−4.66*	3.11*	−0.33	−1.7	0.1	−0.2
2,4-DP	−5.38*	3.36*	−1.2	−1.9	0.5	0.2
2,4-D	−5.20*	2.56*	0.12	−2.8*	0.8	−0.8
2,4,5-TP	−3.15*	0.99	−1.07	−0.6	1.7	−1.1
2,4,5-T	−6.19*	2.47*	−1.37	−1.4	2.4*	0.8
MCPB	−1.91	−1.42	−0.57	−2.3*	4.1*	2.3*
2,4-DB	−0.92	−0.89	−0.18	−2.2	1.7	0.4

* Statistically significant effects at the 95% confidence level.

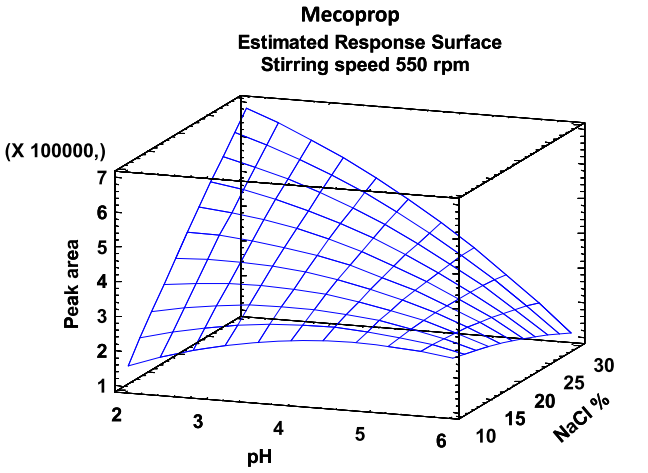

Fig. 1. Surface response plot obtained for mecoprop during optimization of sorptive microextraction conditions.

260 °C (5 min). Transfer line, ion source and quadrupole temperatures were set at 280 °C, 200 °C and 150 °C, respectively. The mass analyzer was operated in the selected ion monitoring mode, with compounds grouped in eight time windows, considering dwell times between 50 and 100 ms per ion. Retention times and recorded ions for silylated herbicides and the IS are provided in Table 1.

3. Results and discussion

3.1. Desorption and derivatization conditions

The selection of the desorption solvent employed to recover the extracted compounds from the PES sorbent considered (1) its compatibility with the polymeric material, and (2) the further use of MTBSTFA as derivatization reagent. As reported elsewhere [25,27], the PES polymer displays a limited stability towards acetone and it is decomposed in contact with chlorinated solvents, as chloroform. On the other hand, polar and protic solvents (e.g. methanol), which are expected to display high affinity for polar analytes, are not compatible with the preparation of silyl derivatives. Thus, ethyl acetate was chosen as desorption solvent and departure silylation conditions were adopted from a previous study [11].

The efficiency of the desorption step was investigated soaking each piece of sorbent (previously exposed to 100 ng mL^{-1} spiked water samples) with three consecutive fractions (0.1 mL each) of ethyl acetate, for 15 min. Normalized responses for the 2nd fraction remained below 5% of those measured for the 1st one and, most of the analytes were not detected in the 3rd desorption step. Since PES tubes were considered as disposable sorbents, 0.1 mL was finally selected as the optimum volume of ethyl acetate.

The potential influence of the derivatization time (2–60 min), temperature (20–60 °C) and MTBSTFA volume (2–20 μL) on the efficiency of the silylation reaction were evaluated using a central composite experimental design (CCD), involving a total of 18 experiments. Peak areas, measured for each compound, were used as variable responses to investigate the main effects associated to each of the above parameters, their quadratic terms, and the two-factor interactions. All compounds displayed the same behaviour and none of the factors exerted a significant influence on the responses measured for their silylated derivatives. However, the interaction time-temperature affected significantly (95% confidence level) the efficiency of the derivatization reaction. The highest responses for all analytes were observed for low temperatures and long reaction times, data not shown. In a previous study, we have also reported a slight diminution in the responses of silyl derivatives of phenoxy acid compounds when using temperatures above 40 °C [11]. Thus, 20 °C and 45 min were selected as optimal values for both variables, whereas the volume of MTBSTFA was maintained at medium level (10 μL). In practice, the derivatization process was carried out at room temperature (18–22 °C), and silylated extracts were analyzed within the next 5 days to prevent back hydrolysis to their free forms [11].

The instrumental limits of quantification (LOQs) for silylated phenoxy acid standards varied between 1 and 8 ng mL^{-1} with

a linear response range up to 1000 ng mL^{-1}. The repeatability of derivatization and determination steps remained below 4%, for a 100 ng mL^{-1} standard, see supplementary information (Table S1).

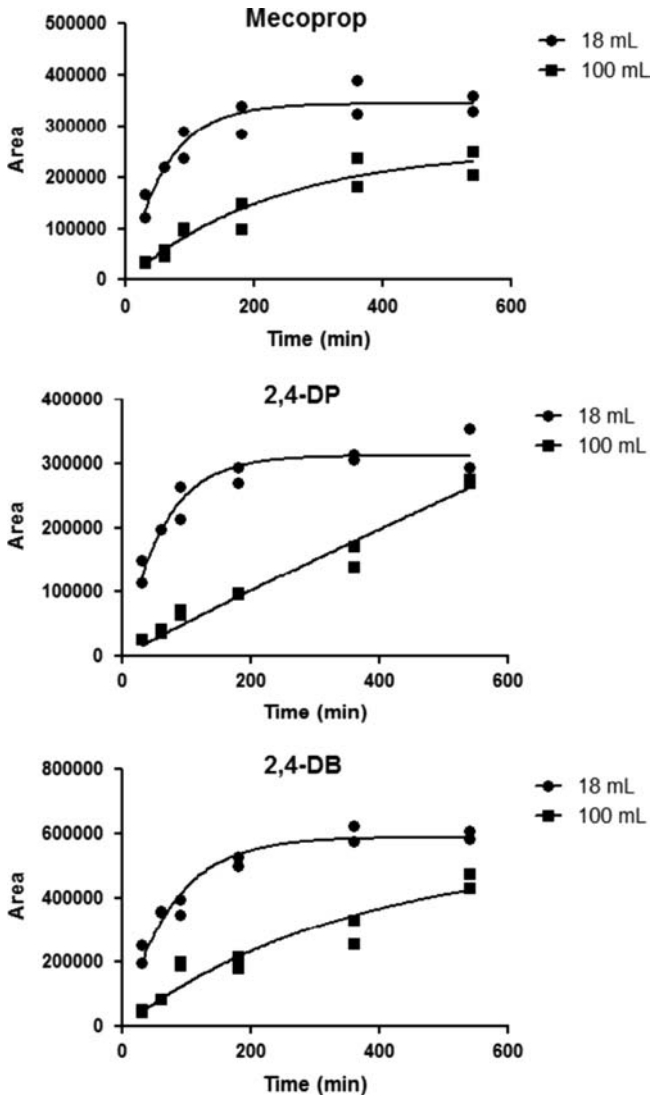

Fig. 2. Time-course of the sorptive microextraction for selected compounds considering 18 and 100 mL volume samples.

3.2. Microextraction conditions

Unless different values are specified, optimization of extraction conditions was performed with spiked (20 ng mL^{-1}) water samples, using 20 mL volume vessels and considering a sampling period of 150 min. In a first series of extractions, samples were adjusted at pH 2 to get all compounds in their neutral forms. Under these conditions, the addition of sodium chloride (NaCl, 20%, w/v) led to a significant increase in the responses of all compounds. Stirring (500 rpm) also improved the yield of the extraction versus non-stirred samples. On the other hand, the use of methanol as organic modifier (5%, v/v) caused a reduction in the extraction efficiency of all target analytes.

In view of these preliminary results, the effects of sample pH, NaCl concentration and stirring speed in the responses of target herbicides were evaluated using a second CCD response surface design, with four replicates of the central point. The range of explored values was 2–6 units (pH), 10–30% (NaCl concentration) and 300–800 rpm (stirring speed). Responses (peak areas) measured for each compound were processed with the Statgraphics Centurion software (Manugistics, Rockville, MD, USA). Table 2 compiles the standardized values of main effects. Their absolute values are proportional to the variation in the responses measured for a given herbicide when the associated variable passes from the low to the high level, within the domain of the design. A positive sign means an improvement in the extraction efficiency, whereas a negative one points out to the opposite trend.

The pH of the sample was the most important variable exerting a negative, and in most cases statistically significant (95% confidence level), influence on the yield of the extraction, Table 2. This pattern is in good agreement with the low p*Ka* values of target compounds and, in fact, the maximum standardized effect associated to pH corresponded to dicamba (the most acidic analyte, p*Ka* 2.40), whilst for phenoxy butanoic acids (MCPB and 2,4-DB; p*Ka* values around 4.6 units) the standardized main effect of this variable remained below the level of statistical significance, Table 2.

The stirring speed was the least important factor, with main effects far below the statistical significance boundary. Although stirring is known to favour the diffusion of the analytes from the sample to the interface with the PES sorbent, such effect was not significant within the range of values (300–800 rpm) considered for this factor in the design, Table 2.

Finally, the percentage of NaCl had a positive effect in the responses of most herbicides, being statistically significant for dicamba, MCPA, 2,4-DP, 2,4-D and 2,4,5-T.

Standardized values for two-factor interactions are also summarized in Table 2. In some cases, they were statistically

Table 3
Performance of the developed method.

Compound	Linearity (R^2, 0.05–5 ng mL^{-1}, n=6 levels)	Intra-day precision (RSDs %, n=5 replicates)		Inter-day precision (RSDs %, n=9 replicates, 3 days)	LOQs (ng mL^{-1})	EE (%) ± SD n=5 replicates
		0.20 ng mL^{-1}[a]	0.02 ng mL^{-1}[a]	0.6 ng mL^{-1}[a]		
Mecoprop	0.994	8	10	9	0.017	54 ± 1
Dicamba	0.993	10	8	15	0.005	39 ± 2
MCPA	0.995	13	5	11	0.009	50 ± 4
2,4-DP	0.992	5	7	15	0.018	55 ± 3
2,4-D	0.991	6	4	5	0.019	45 ± 8
2,4,5-TP	0.991	11	[b]	10	0.069	55 ± 2
2,4,5-T	0.992	9	[b]	13	0.073	42 ± 6
MCPB	0.999	6	9	10	0.01	62 ± 7
2,4-DB	0.997	6	7	13	0.02	66 ± 3

[a] Added concentration.
[b] Below LOQs.

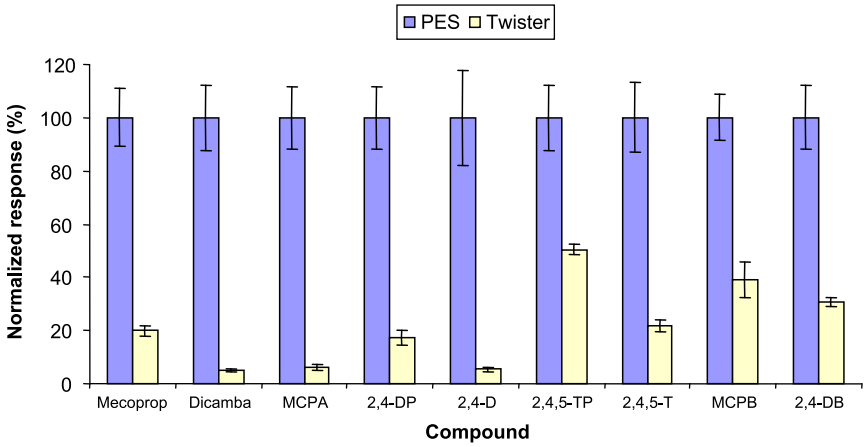

Fig. 3. Comparison between extraction efficiencies provided by PES membranes (polymer volume 8 μL) and PDMS coated *Twisters*™ (PDMS coating 24 μL), $n=3$ replicates.

Table 4
Comparison of main features corresponding to microextraction methods applied to phenoxy acids extraction from water samples.

Extraction technique	Extraction time (min)[a]	Sample volume (mL)	Simultaneous extractions	Determination technique	Number of analytes	LOQs (ng mL^{-1})	Ref.
SPME (PA)	40	20	No	GC–MS	9	0.004–0.028	[19]
SPME (PA)	50	25	No	GC–MS	8	0.03–0.09[b]	[18]
SPME (PDMS)	20	1.2	No	GC–MS	4	0.6–6.6[b]	[20]
SPME (PDMS-DVB)	60	3	No	GC–MS	4	0.3–3[b]	[21]
SBSE (PDMS)	240	15	Yes	GC–MS	7	0.05–1.3[b]	[22]
In-tube SPME	Not available	10	No	LC–MS/MS	6	0.02–0.06	[17]
Cloud point LPME	60	10	Yes	GC–MS	2	0.0024–0.0091[b]	[23]
HF-LPME	9	1	No	LC–UV	5	0.3–1.2[b]	[4]
PES sorptive extraction	180	18	Yes	GC–MS	9	0.005–0.073	This work

[a] Without considering the derivatization step.
[b] Reported LODs were multiplied by a factor of 3.

Table 5
Relative recoveries of the microextraction process with PES sorbents for different water samples, $n=3$ replicates.

Compound	Recovery (%) ± SD			
	River water 0.2 ng mL^{-1}[a]	River water 0.6 ng mL^{-1}[a]	Sewage 0.2 ng mL^{-1}[a]	Sewage 0.6 ng mL^{-1}[a]
Mecoprop	91 ± 7	86 ± 8	83 ± 8	120 ± 9
Dicamba	101 ± 6	80 ± 5	73 ± 7	86 ± 2
MCPA	91 ± 9	101 ± 7	74 ± 7	109 ± 5
2,4-DP	107 ± 4	86 ± 9	104 ± 17	104 ± 5
2,4-D	116 ± 8	116 ± 6	90 ± 6	108 ± 3
2,4,5-TP	103 ± 7	90 ± 10	100 ± 15	98 ± 9
2,4,5-T	97 ± 2	114 ± 4	88 ± 5	100 ± 5
MCPB	115 ± 4	113 ± 4	91 ± 5	105 ± 7
2,4-DB	103 ± 2	117 ± 5	73 ± 3	119 ± 10

[a] Added concentration.

significant (95% confidence level). Overall, the higher absolute values corresponded to the interaction sample pH-NaCl concentration, meaning that the positive effect of increasing the ionic strength of the sample in the extraction efficiency was observed only at low pHs, when herbicides are in their neutral forms. At pH 6, the extraction of the negatively charged species was scarcely affected by the concentration of NaCl. Finally, the quadratic terms for the three variables involved in the CCD design remained below the level of significance for all compounds, data not given.

On the basis of the above results, further extractions were performed with samples containing a 30% of NaCl, adjusted at pH 2 and stirred at 550 rpm. As depicted exemplarily in the surface response graph for mecoprop (Fig. 1), these conditions maximized the obtained responses.

The influence of the volume of sample on the efficiency and on the kinetics of the microextraction were assessed for 18 and 100 mL samples (both spiked at the 2 ng mL^{-1} level) placed in 22 and 90 mm diameter glass vessels, with total capacities of 20 and 110 mL, respectively. Duplicate extractions were performed at different times, between 0.5 and 9 h. Fig. 2 shows the time-course of the extraction process for mecoprop, 2,4-DP and 2,4-DB (the rest of compounds displayed similar profiles). In case of

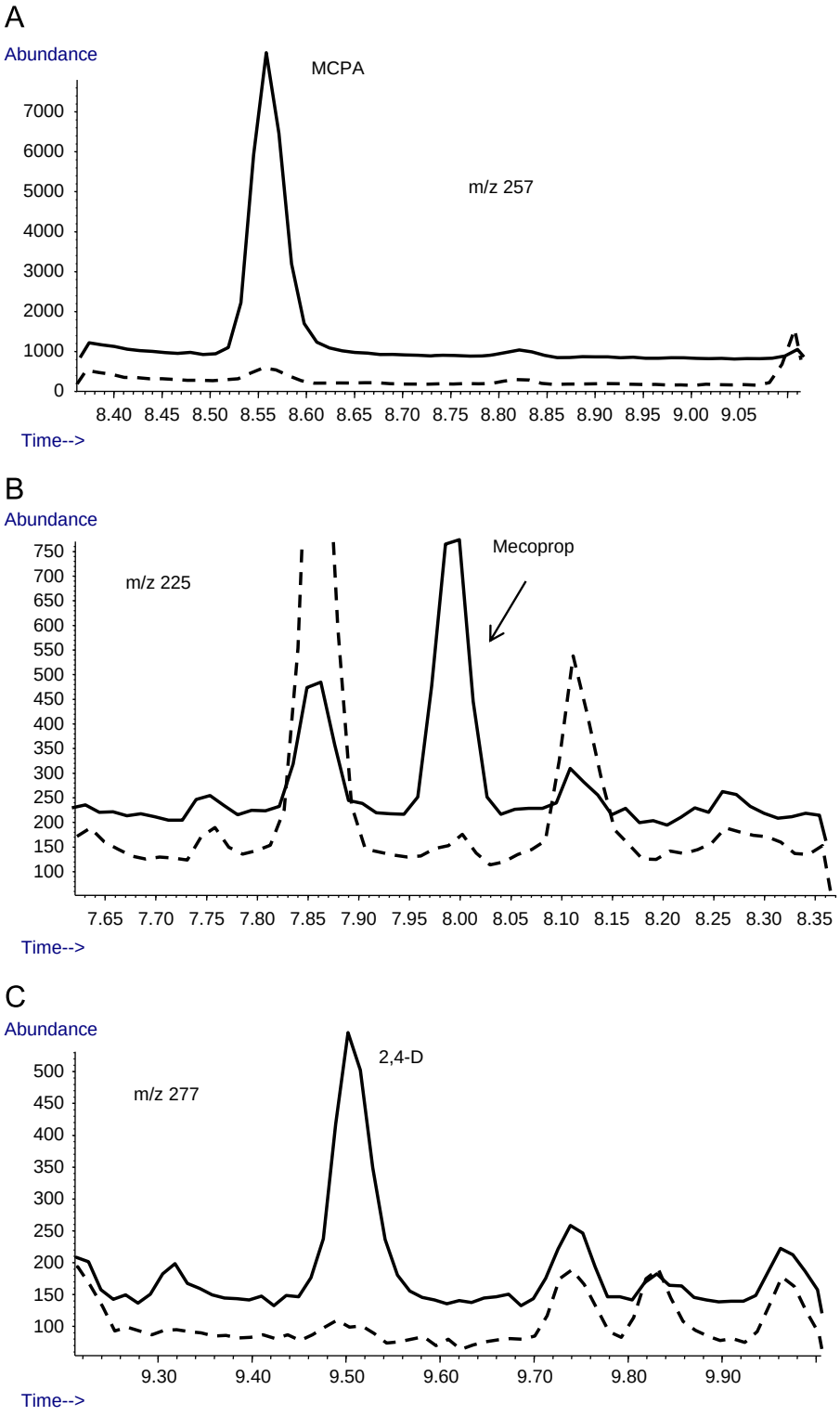

Fig. 4. GC–MS chromatograms corresponding to a positive surface water sample (solid line) and a procedural blank (dotted line). (A) MCPA (1.52 ng mL^{-1}). (B) Mecoprop (0.032 ng mL^{-1}). (C) 2,4-D (0.062 ng mL^{-1}).

100 mL samples, responses increased steady with time, suggesting that equilibrium was not achieved within the investigated extraction period. On the contrary, for 18 mL samples, responses remained basically constant after 180 min. Within the selected time interval, higher responses were measured for lower sample volumes, suggesting a more efficient mass transfer kinetics. Thus, the 20 mL vessels, containing 18 mL volume samples, were kept for further experiments and the extraction time was fixed at 180 min, with samples being simultaneously concentrated in a 12-possitions magnetic stirring plate.

3.3. Method performance and real samples analysis

Table 3 compiles the data related to the performance of the optimized method. Linearity was evaluated with water aliquots spiked at six different concentration levels, prepared in duplicate,

in the range between 0.05 and 5 ng mL^{-1}, with the IS maintained at 0.5 ng mL^{-1}. Determination coefficients (R^2) for the corresponding plots (analyte peak area/IS peak area versus concentration) varied between 0.991 and 0.999. Intra- and inter-day precision were investigated with samples spiked at three different concentrations. After IS normalization, relative standard deviations (RSDs) were 4–13% and 5–15% under repeatability (intra-day) and reproducibility (inter-day) conditions, respectively, Table 3. The LOQs of the method were calculated as the concentration of each compound providing a chromatographic peak with a height 10 times higher than the standard deviation of baseline noise in procedural blanks, measured at the retention time of each species [17]. Achieved values varied from 0.005 ng mL^{-1} for dicamba to 0.073 ng mL^{-1} for 2,4,5-T.

The absolute extraction efficiency (*EE*, %) of the method was evaluated with spiked (2 ng mL^{-1}) aliquots of ultrapure water, extracted under conditions described in the above paragraphs. *EE* values were calculated as $EE = C_e/C_t \times 100$. C_e is the concentration measured for each compound in the extracts from PES sorbents. Its value was determined against calibration curves obtained for standards in ethyl acetate, derivatized under same conditions as sample extracts. C_t represents the theoretical concentration of the extracts, assuming quantitative recoveries of target analytes and taking into account the ratio between sample and extract volumes (18 and 0.1 mL, respectively). Extraction recoveries varied from 39% for dicamba up to 66% for 2,4-DB, Table 3. These values are relatively high for a microextraction technique, particularly considering the large difference between sample and sorbent volumes (18 and 0.008 mL, respectively).

To further demonstrate the affinity of the PES sorbent for polar analytes involved in this study, its extraction efficiency was compared to that provided by PDMS covered *Twisters*™ (coating volume 0.024 mL). To allow a direct comparison between both sorbents, the desorption step was slightly modified up-scaling 10 times the volumes of ethyl acetate (1 mL) and derivatization reagent (0.1 mL of MTBSTFA). Such modifications were required due to the much larger volumes of *Twisters* (comprising the PDMS coating plus the PTFE stir bar) versus PES membranes. The relative extraction yields obtained with *Twisters* remained between 5% and 50% of those provided by PES (Fig. 3), despite the three-fold lower volume corresponding to the latter sorbent.

Table 4 compares some relevant features of different microextraction techniques with those obtained in this work. Attained LOQs remained at the same level as those corresponding to SPME, using PA fibres followed by *on-fibre* derivatization of the analytes [18,19], *in-tube* SPME combined with LC–MS/MS [17] and were slightly higher to those reported for MCPA and Mecoprop by cloud point LPME [23]; however, the suitability of this latter technique for wastewater samples was not reported. Extractions required 3 h, which is longer than the sampling time used in most microextraction techniques, except in case of SBSE [22]; however, this feature does not represent a relevant drawback since extractions are simultaneously performed in an unattended way. Moreover, at difference to SPME, in-tube SPME and HF-LPME, the developed method provides enough extract volume to be re-analyzed, if required, without repeating the whole sample preparation.

The effect of the sample matrix in the efficiency of the microextraction was evaluated with raw sewage and river water, spiked at two different concentration levels (0.2 and 0.6 ng mL^{-1}). Differences between the responses (analyte/IS peak area) measured for spiked and non-spiked fractions ($n=3$ replicates) of the above samples were divided by those observed for ultrapure water aliquots, spiked at the same levels, and multiplied by 100. In the case of surface water, the relative recoveries varied between 80 and 117%, with standard deviations below 10%, Table 5. For the most complex raw sewage sample, similar recoveries were measured (73–120%); although, their associated standard deviations raised up to 17%, Table 5. Therefore, after IS correction, the performance of the extraction process was only moderately affected by the characteristics of different water samples. Consequently, pseudo-external calibration, with spiked aliquots of ultrapure water, can be considered as a suitable quantification strategy, without the need of using the time-consuming standard addition procedure.

The presence of phenoxy acid residues was investigated in 24-h integrated samples of raw wastewater, from a 100,000 inhabitant city, obtained during a week. None of the compounds was detected in this matrix at levels above the LOQs of the method. On the other hand, some of the herbicides were found in surface water samples, obtained from small creeks flowing through a rural area and collected at the end of spring. The highest detected level corresponded to MCPA, with a concentration of 1.52 ± 0.07 ng mL^{-1}. Mecoprop and 2,4-D were also found in the same sample at concentrations of 0.032 ± 0.001 ng mL^{-1} and 0.062 ± 0.004 ng mL^{-1}, respectively, Fig. 4. These values are similar to those reported in seawater [23] and significantly lower than the 40 ng mL^{-1} level of 2,4-D found in pond water samples collected in the vicinity of gardening areas [24].

4. Conclusions

An alternative method for the concentration and extraction of nine acidic herbicides from aqueous samples using low-cost PES sorptive extraction followed by GC–MS, after liquid desorption and derivatization (silylation), was developed. Under optimized conditions, the PES sorbent provided absolute extraction efficiencies between 39 and 66%, achieving quantification limits from 0.005 to 0.073 ng mL^{-1} similar to, or even better than, those reported for commercial microextraction techniques. Simplicity of the procedure, small solvent volume consumption and low overall cost, together with the scarcely affection of the yield in the whole procedure by the type of water sample, are the main advantages of the present methodology. Globally, the figures of merit of the method confirm the suitability of PES membranes for phenoxy acids microextraction from water samples. Since analytes are recovered as non-derivatized species, the extraction procedure is also susceptible of combination with LC–MS/MS.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.01.024.

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