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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 \times 0.7 mm o.d., sorbent volume 8 μ L). 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.

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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 chloroformates 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-d₃-acetic-2,2-d₂ acid (2,4-D-d₅), 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

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