Improving the On-Line Extraction of Polar Compounds by IT-SPME with Silica Nanoparticles Modified Phases

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Abstract: In the present work the extraction efficiency of in-tube solid-phase microextraction (IT-SPME) for polar herbicides has been evaluated using extractive capillaries coated with different polymeric sorbents. For this purpose, aqueous solutions of herbicides with a wide range of polarities, including some highly polar compounds (log K_{ow} < 1), have been directly processed by IT-SPME coupled on-line to capillary liquid chromatography with UV-diode array detection. For extraction, commercially available capillary columns coated with polydimethylsiloxane (PDMS) and polyetilenglicol (PEG)-based phases have been used, and the results have been compared with those obtained with a synthesized tetraethyl orthosilicate (TEOS)-trimethoxyethylsilane (MTEOS) polymer, as well as the same polymer reinforced with silica nanoparticles (SiO_2 NPs). The SiO_2 NPs functionalized TEOS-MTEOS coating provided the best results for most herbicides, especially for the most polar compounds. On the basis of the results obtained, conditions for the quantification of the herbicides tested are described using a SiO_2 NPs reinforced TEOS-MTEOS coated capillary. The proposed method provided satisfactory linearity up to concentrations of 200 µg/L. The precision was also suitable, with relative standard deviations (RSDs) values ≤9% (*n* = 3), and the limits of detection (LODs) were within the 0.5–7.5 µg/L range. The method has been applied to different water samples and the extract obtained from an agricultural soil.

Keywords: in-tube solid-phase microextraction (IT-SPME); polar herbicides; capillary liquid chromatography; SiO_2 nanoparticles

1. Introduction

In spite of the recent advances in sample preparation, the extraction of polar pollutants from aqueous matrices is still one of the major challenges in environmental analysis. Polar organic pollutants cause great concern because of their wide distribution in water compartments and potential toxicity. Among them, herbicides are of particular interest because large amounts of these compounds are constantly deposited in crops and soils, entering the atmosphere and natural waters through a variety of pathways. In order to minimize their negative impact on the environment, modern pesticides have been designed with higher effectiveness and improved selectivity (so they can be applied at lower doses), as well as faster degradability. Also, to minimize bioaccumulation modern pesticides are increasingly polar. Therefore, sample preparation methodologies have to be adapted to these properties [1].

In-tube solid-phase microextraction (IT-SPME) has proved to be a reliable alternative for the on-line enrichment of many organic pollutants from aqueous matrices prior to their analysis by liquid
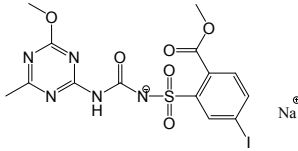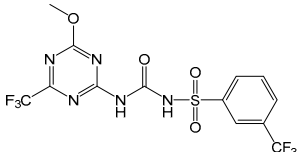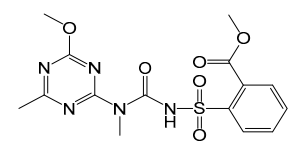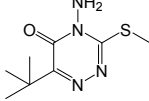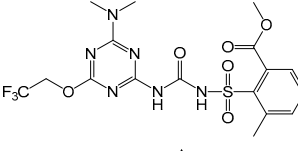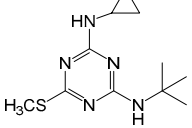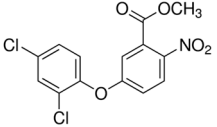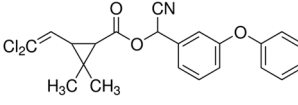
chromatography (LC). This is because it allows the accumulation of the amount of analyte required to generate an instrumental response simply by introducing large volumes of the samples in the extractive device [2,3]. As an extractive device, a capillary column coated (or packed) with the proper sorbent can be used in replacement of the inner loop of the injection valve (in-valve IT-SPME), so that the target compounds are extracted during sample loading, and desorbed and transferred to the separative column somewhat later with the mobile-phase. Segments of coated capillary columns from gas chromatography (GC) were primarily used as extractive capillaries. However, in order to enhance the efficiency and selectivity of the extraction, great efforts are being paid in the development of new coatings.

Over the past years different types of sorbents have been explored for extraction and microextraction, polymeric and nanostructured sorbents being the most commonly used so far [4–6]. A variety of polymeric sorbents have been synthesized using different strategies (electro-polymerization, sol-gel), including molecularly imprinter polymers (MIPs). These materials offer suitable results for several types of compounds through a variety of interaction mechanisms, from relative unspecific hydrophobic or van der Waals forces to highly selective interactions such as those involved in MIPs-mediated extractions [4,5]. Nanostructured materials are also very attractive in microextraction mainly because they provided high specific area for interaction, thus high extraction efficiencies can be attained. In addition, in many cases their surface can be chemically modified in order to increase the affinity for the target compounds. Nanomaterials are increasingly used in different sample preparation techniques [6,7], although the number of applications described for IT-SPME is still limited. Successful examples include the TiO_2 nanoparticles (NPs) coated capillaries synthesized by Lin and coworkers for the isolation of phosphopeptides from protein digests [8]. Feng and coworkers prepared a coating by graphting poly(*N*-isopropyl acrylamide) (PNIPPAm) on a capillary previously coated with SiO_2 NPs [9]; compared to capillaries directly coated with PNIPAAm, the presence of the silica NPs provided higher specific surface area, and more surface coverage of PNIPAAm, which in turn resulted in improved extraction capability for different estrogens. A magnetic hybrid material formed by Fe_3O_4 NPs supported on silica immobilized in the surface of a fused silica capillary was used to develop the so-called magnetic IT-SPME [10]. The utility of this methodology has been demonstrated for different kind of pollutants and pharmaceuticals [10,11].

From another perspective, NPs can be embedded into a polymeric coating in order to introduce additional interaction mechanisms with the compounds of interest. For example, in previous works we demonstrated that the functionalization of commercially available polydimethylsiloxane (PDMS)-based coatings with carbon nanotubes (CNTs) led to a significant improvement of the extraction efficiency for some drugs and pollutants mainly via π-π interactions [12–14]. Unfortunately, this approach failed in improving the extraction efficiency of highly polar compounds [13]. More recently, an organic modified silica coating (tetraethyl orthosilicate (TEOS)-trimethoxyethylsilane (MTEOS)) reinforced with SiO_2 NPs has proved to be effective the extraction of three relatively polar pollutants (log K_{ow} 2.3–3.2) [15].

As a continuation of those studies, in the present work we have evaluated different coatings for the extraction of herbicides with a wide range of polarities, including some highly polar pesticides (log K_{ow} < 1). The compounds tested and their log K_{ow} are listed in Table 1. The extraction efficiency of commercially available capillaries coated with PDMS- and polyetilenglicol (PEG)-based polymers have been compared with those achieved with capillary coated with TEOS-MTEOS and TEOS-MTEOS reinforced with SiO_2 NPs. Based on the results obtained, conditions for the quantification of the tested herbicides are proposed using a SiO_2 NPs reinforced TEOS-MTEOS phase for IT-SPME. The analytical performance of the proposed approach and possible applications within the environmental samples are discussed.

Table 1. Chemical structures of the tested compounds and their respective log K_{ow} (values taken from the literature).

Compound	TRB 35	Log K_{ow}	Reference
Iodosulfuron-methyl-sodium		−0.7	[16]
Tritosulfuron		0.6	[17]
Tribenuron-methyl		0.8	[18]
Metribuzin		1.7	[18]
Triflusulfuron-methyl		3.1	[16]
Irgarol		3.1	[19]
Bifenox		4.4	[18]
Cypermethrin		6.6	[18]

2. Materials and Methods

2.1. Chemicals

All reagents were of analytical grade. Iodosulfuron-methyl-sodium, tribenuron-methyl, tritosulfuron, triflusulfuron-methyl, metribuzin, irgarol 1051®, bifenox, cypermethrin (mixture of isomers), tetraethyl orthosilicate (TEOS), triethoxymethylsilane (MTEOS), poly(ethylene glycol) (PEG), SiO$_2$ NPs (5–15 nm), NaOH and NH$_4$OH were obtained from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile was of HPLC grade (VWR, Radnor, PA, USA).

Stock standard solutions of the analytes (100 µg/mL) were prepared by dilution of the commercial reagents in acetonitrile and kept at −20 °C until use. Working solutions were prepared by dilution of the stock solutions with ultrapure water.

2.2. Apparatus and Chromatographic Conditions

The chromatographic separations were performed using a capillary chromatographic system consisting of a binary capillary pump (Agilent Series 1000, Waldbron, Germany), a six-port injection valve and a UV-diode array detector (Agilent, 1200 series, Waldbron, Germany) equipped with an 80 nL flow cell. The detector was coupled to a data system (Agilent, HPLC ChemStation, Waldbron, Germany) for data acquisition and treatment. The analytical signal was recorded between 190 and 400 nm, and monitored at 230 nm. For the chromatographic analysis, a Zorbax SB C18 (150 mm × 0.5 mm i. d., 5 μm) column (Agilent, Waldbron, Germany) was used. For separation of the sulfonylurea herbicides iodosulfuron-methyl-sodium, tribenuron-methyl, tritosulfuron and triflusulfuron-methyl, the mobile phase was a mixture water-acetonitrile in gradient elution mode: the percentage of acetonitrile was increased from 20% at 0–10 min to 55% at min 15, and then to 70% at min 30; the mobile-phase flow rate was 8 μL/min. For the chromatographic analysis of the other herbicides included in this study, the mobile-phase was a mixture of water-acetonitrile 20:80 (*v*/*v*) at a flow rate of 6 μL/min. All solvents were filtered through 0.22 μm nylon membranes (Teknokroma, Barcelona, Spain) before use. All the assays were performed in triplicate at room temperature.

2.3. Preparation of the TEOS-METEOS Coated Capillaries

The TEOS-MTEOS coated capillaries were prepared using 30 cm-segments of fused silica capillaries, 320 μm o. d. and 75 μm i. d. (Análisis Vínicos, Tomelloso, Spain) with a procedure described in detail in [15]. Briefly, the internal walls of the silica capillaries were first activated by flushing through them 1 M NaOH for 4 h at 40 °C followed by 0.1 M HCl for 30 min at room temperature; next, the capillaries were heated at 60 °C for 3 h, and finally flushed with water and dried with air. For coating of the capillaries, a mixture of 65 mg of PEG, 100 μL of TEOS, 100 μL MTEOS, 50 μL of water and 2 mL of 0.1 M NH_4OH (catalyst) were mixed in a glass vial; after vortexing for 1 min, the resulting homogenous dispersion was used to fulfill the preconditioned capillaries. Then, the capillaries were heated at 40 °C for 2 h and aged overnight (14–15 h) at 120 °C. The same procedure was used to prepare the SiO_2 NPs functionalized capillaries, but the NPs were incorporated to TEOS/MTEOS mixture; the amount of NPs in the suspension was 0.05 mg/mL, as in [15].

2.4. IT-SPME Conditions

30 cm length segments of different commercially available GC columns (0.32 mm, i. d.) were used as extractive capillaries for IT-SPME, namely TRB 5, TRB 35, ZB-WaxPlus and ZB-FFAP, and the results were compared with those synthesized with TEOS-MTEOS and SiO_2 NPs reinforced TEOS-MTEOS. The TRB 5 and TRB 35 capillaries, coated with a 5% diphenyl-95% PDMS and 35% diphenyl-65% PDMS, respectively, both 3 μm coating thickness, were purchased from Teknokroma (Barcelona, Spain). The PEG-based ZB-WaxPlus capillary and the ZB-FFAP (nitroterephthalic acid modified PEG), both coated with 1 μm film thickness, were supplied from Phenomenex (Torrance, CA, USA). A schematic representation of the different phases tested is given in Table 2.

The on-line preconcentration by IT-SPME was effected under an in-valve configuration. For this purpose the extractive capillary was used as the loop of the six-port injection valve. Samples were manually loaded into the extractive capillary using a 500 μL precision syringe; then, the valve was changed to the injection position, so the analytes retained in the capillary were desorbed with the mobile-phase and transferred to the analytical column for separation and detection. For connecting the extractive capillaries to the valve 2.5 cm sleeve of 1/6 i. n. (340–380 μm i. d.) polyether ether ketone (PEEK) tubing, 1/6 i. n. PEEK nuts and ferrules were used. The fused silica capillaries were put inside the sleeves; then, the sleeves were placed inside standard ferrules and screwed on the valve. All assays were made by triplicate.

Table 2. Structure of the polymeric coatings tested.

Extractive Phase	Structure
PDMS [1]	
PEG	
	FFAP
TEOS-MTEOS	

[1.] TRB 5: a = 95, b = 5; TRB 35: a = 65, b = 35.

2.5. Analysis of Environmental Samples

Two transition water samples and three seawater samples collected at different points along the coastline of the Comunitat Valenciana region (East Spain) were analyzed. Once collected, samples were kept at 4 °C, and filtered 0.22 μm nylon filters (Teknokroma) just before their analysis.

For the analysis of soil, a soil sample collected from an agricultural zone was dried at ambient temperature and then sieved ($\leq$2 μm). Accurately weight portions (1.0 g) were spiked with the analytes and extracted with 4 mL of methanol at 30 °C in an ultrasonic bath for 30 min. After centrifugation at 5000 rpm, the supernatant was removed and filtered with 0.22 μm nylon filters (Teknokroma). The filtered extracts were evaporated to dryness and then reconstituted with 200 μL of ultrapure water. Finally, 100 μL of the reconstituted extracts were processed under the proposed conditions. All assays were made by triplicate.

3. Results

Initially, the chromatographic profiles obtained with the different extractive capillaries coatings tested were evaluated. Similar peak profiles and retention times were found for the target compounds with all the extractive capillaries tested. This indicates that for all the coatings assayed the desorption and transfer of the analytes from the extractive capillary to the analytical column with the mobile phases was very rapid and thus, the inclusion of the IT-SPME device did not cause additional peak broadening. Two peaks were found for cypermethrin under a variety of elution conditions, which were attributed to the presence of isomers in the commercial reagent. For quantitative purposes the sum of areas of the two peaks was used as the analytical signal.

3.1. Study of the Extraction Efficiencies

In order to compare the extractive performance of the different capillaries, aliquots of 100 μL of solutions containing the analytes at concentrations of 200 μg/L were processed and the peak areas were measured. The results obtained are depicted in Figure 1.
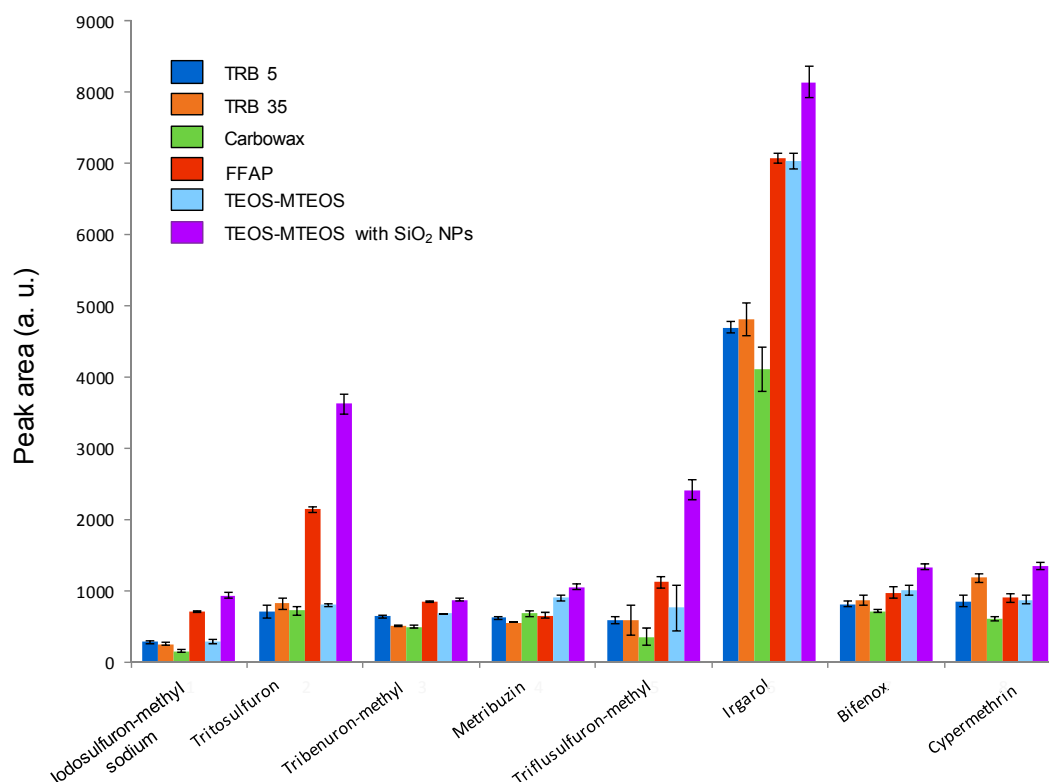
Figure 1. Peak areas obtained with the tested capillary coatings (*n* = 3). Concentration of the analytes, 200 µg/L.

In order to check if the increment on peak areas obtained with the SiO$_2$ NPs modified TEOS-MTEOS coating were significantly different from those achieved with other coatings, a *t* test was applied. For this purpose, *t* was calculated for the two coatings that provided the highest peak areas for each analyte. In other words, the peak areas obtained with the SiO$_2$ NPs reinforced TEOS-MTEOS coating were compared with the areas obtained with the FFAP coating for iodosulfuron-methyl-sodium, tritosulfuron tribenuron-methyl, triflusulfuron-methyl and irgarol, with the TEOS-MTEOS coating for metribuzin and bifenox, and with the TRB 35 coating for cypermethrin (Figure 1). The t$_{calculated}$ values were higher than the t$_{tabulated}$ at 95% confidence level except for tribenuron-methyl (t$_{calculated}$ = 1.485; t$_{tabulated}$ = 2.365). This means that the SiO$_2$ NPs-TEOS/MTEOS coating provided statistically different (higher) peak areas, except for tribenuron-methyl.

In order to compare the extraction efficiency of the different extractive coatings, the enrichment ratios (ERs) were obtained for each analyte. These values were calculated as the peak area ratios obtained with each coating to those measured with the PDMS TRB 5 capillary. The TRB 5 capillary coating was selected as reference because this was the capillary used in previous studies with polar herbicides [13]. The results obtained are listed in Table 3.

Table 3. Enrichment ratios obtained with respect the TRB 5 capillary columns.

Compound/ER	TRB 35	PEG	FFAP	TEOS-MTEOS	TEOS-MTEOS with SiO$_2$ NPs
Iodosulfuron-methyl-sodium	0.90 ± 0.09	0.55 ± 0.08	2.5 ± 0.2	1.0 ± 0.1	3.3 ± 0.02
Tritosulfuron	1.1 ± 0.2	1.0 ± 0.1	3.0 ± 0.4	1.1 ± 0.1	5.1 ± 0.6
Tribenuron-methyl	0.79 ± 0.03	0.77 ± 0.04	1.8 ± 0.1	1.06 ± 0.03	3.8 ± 0.1
Metribuzin	0.90 ± 0.02	1.10 ± 0.07	1.06 ± 0.07	1.46 ± 0.07	1.8 ± 0.1
Triflusulfuron-methyl	1.0 ± 0.4	1.0 ± 0.2	1.9 ± 0.2	1.3 ± 0.6	4.1 ± 0.4
Irgarol	1.03 ± 0.05	1.08 ± 0.07	1.25 ± 0.03	1.50 ± 0.04	2.6 ± 0.1
Bifenox	1.1 ± 0.1	1.10 ± 0.05	1.3 ± 0.1	1.2 ± 0.1	2.1 ± 0.1
Cypermethrin	1.3 ± 0.2	0.65 ± 0.08	1.5 ± 0.1	1.4 ± 0.1	2.1 ± 0.2

It is known that PDMS based coatings are non-polar, and therefore, hydrophobic interactions with the analytes are predominant. Thus, they may be unsuitable for the extraction of polar compounds. The introduction of diphenyl groups, as in the TRB coatings used in the present study, may improve the extraction efficiency for compounds with aromatic rings due to π-π interactions. Despite most of the tested compounds have aromatic rings (Table 1), the ERs values of Table 3 for the TRB 35 capillaries were close to 1 for all the analytes. Therefore, no significant differences were observed between the extraction efficiencies when using PDMS coatings with 5% and 35% of diphenyl (see Table 3). This suggests that a 5% of diphenyl groups in the extractive phase provided enough points for interaction with the aromatic groups of the analytes.

In PEG-based coatings, the polymeric network is also non-polar, but some hydroxyl groups that remain in the extractive coatings enhance the selectivity for polar compounds [20,21]. In the present study all the target analytes contain functional groups that can interact with –OH (–NH–, –NH₂, …)
(see Table 1). However, the ERs of Table 3 indicate that the extraction efficiencies of PEG are similar of even lower than those obtained with PDMS. This means that the presence of free –OH groups in the PEG coating does not compensate the lack of π-π interactions that can be established between the aromatic structures of the analyes and the diphenyl groups of the TRB phases. This is in agreement with the ERs found with the FFAP phase (nitroterephthalic acid modified PEG). The later capillary coating provided ERs >1.0 for the analytes tested, which can be explained by the presence of aromatic rings in the FFAP phase (see Table 2); the additional functional groups (nitro-, carbonyl-) could also facilitate the interaction with the analytes via hydrogen bonding and dipole-dipole interactions.

When using the synthesized TEOS-MTEOS coating, slightly higher efficiencies were observed with respect the PDMS-based coatings for all analytes, suggesting that hydrophobic interactions are also predominant [22]. This is consistent with the fact that the highest ERs values were obtained for the analytes with highly hydrophobic *t*-butyl moiety, metribuzin and irgarol. Finally, the reinforcement of the TEOS-MTEOS polymer with SiO_2 NPs increased the extraction efficiency for all the compounds, although the higher ERs were found for the most polar analytes. The increment in the extraction efficiency can be explained by the presence of –OH groups in the surface of the SiO_2 NPs [23,24]. Thus, for this coating the extraction efficiency appears as the combination of hydrophobic interactions with the polymeric network and dipole-dipole interactions that can be established between the analytes and free –OH groups on the surface of the trapped NPs.

According to the values of Table 3, a TEOS-MTEOS capillary coating reinforced with SiO_2 NPS was selected for further work. In Figure 2 are depicted the chromatograms obtained for standard solutions of the analytes with the proposed conditions.

3.2. Analytical Parameters

The analytical performance of the synthesized SiO_2 NPs reinforced TEOS-MTEOS was evaluated by processing standard solutions of the tested herbicides up to concentrations of 200 µg/L. The values obtained are summarized in Table 4. As observed from this table, satisfactory linearity was observed within the tested concentration intervals. The precision found was also satisfactory, with RSDs values within the 1–9% interval (*n* = 3). The limits of detection (LODs), established as the concentration of the analytes that resulted in signal-to-noise ratio of 3, were ≤1.0 µg/L for most compounds, although a LOD of 7.5 µg/L was obtained for cypermethrin most probably due to the fact that this compound eluted as a double peak. For cypermethrin, the first eluting peak was used to establish the LOD but this value corresponds to total concentration of isomers.
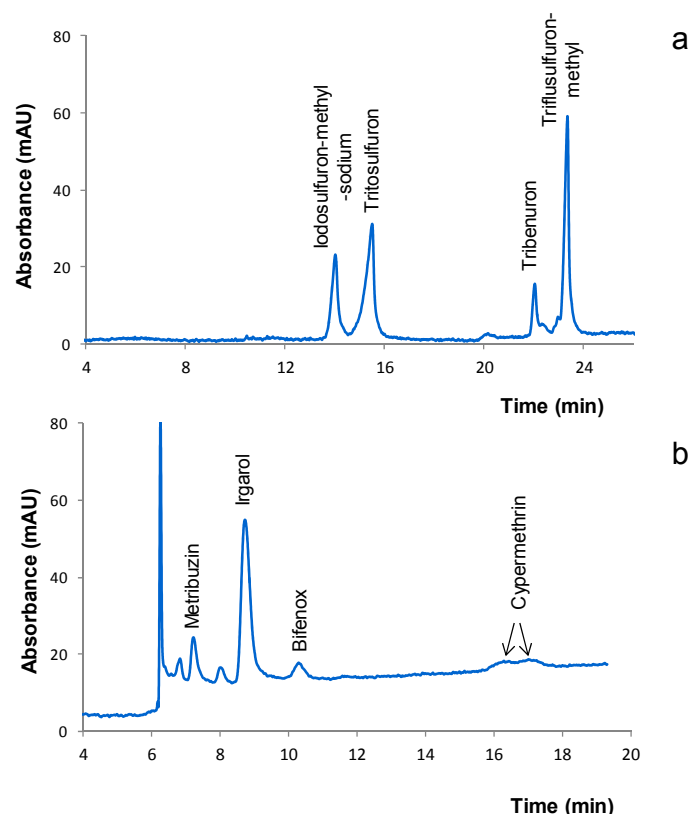
Figure 2. Chromatograms obtained under the proposed conditions for standard solutions of the analytes: (**a**) iodosulfuron-methyl-sodium, tritosulfuron, tribenuron-methyl and triflusulfuron-methyl (100 µg/L each); (**b**) metribuzin, irgarol, bifenox and cypermethrin (25 µg/L each).

Table 4. Analytical parameters obtained with the silica nanoparticles (SiO$_2$ NPs) reinforced tetraethyl orthosilicate (TEOS)-trimethoxyethylsilane (MTEOS) capillary column.

Compound	Linearity [1] y = a + bx			Precision [2] n = 3 CV (%)	LODs µg/L
	a ± Sa	b ± Sb	R^2		
Iodosulfuron-methyl-sodium	−11 ± 2	3.7 ± 0.1	0.990	4	1.0
Tritosulfuron	2 ± 6	5.0 ± 0.2	0.991	2	1.0
Tribenuron-methyl	−17 ±11	6.1 ± 0.1	0.996	3	2.5
Metribuzin	22 ±1	5.17 ± 0.01	0.9990	9	0.5
Triflusulfuron-methyl	−19± 12	6.65 ± 0.10	0.995	3	0.75
Irgarol	−50 ± 30	40.9 ± 0.4	0.9995	1	0.5
Bifenox	−50 ± 40	6.9 ± 0.2	0.9998	5	1.0
Cypermethrin	12 ± 9	5.6 ± 0.2	0.9990	4	7.5

[1] Established for five concentrations within the interval 25–200 µg/L for cypermethrin and 5–200 µg/L for the rest of compounds. [2] Established for a concentration cypermethrin of 100 µg/L and 25 µg/L for the rest of compounds.

3.3. Application to Environmental Samples

In order to test the reliability of the proposed conditions, different transition and sea water samples were processed. The only previous treatment applied to the samples was filtration. None of the herbicides assayed were found in the analyzed samples. Most of the matrix components eluted within 2–6 min, and thus, they did not interfere with the compounds of interest. However, in some of the samples, a peak was observed at a retention time close to that of bifenox; the unknown substance could be unambiguously differentiated from bifenox through its UV spectrum.

Some of the samples were spiked to contain the analytes in order to study the extraction efficiency. As an example, in Figure 3 are shown the spectra obtained for one of the sample and the same sample spiked with some of the analytes assayed.
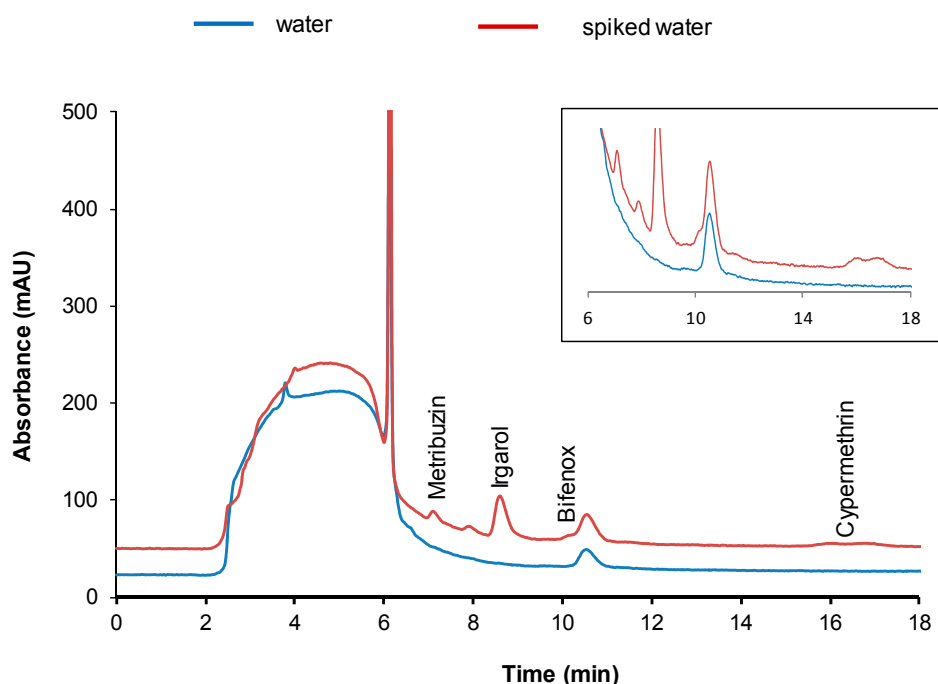

Figure 3. Chromatograms obtained under the proposed conditions for a real water sample and the sample spiked with metribuzin, irgarol, bifenox (25 µg/L), and cypermethrin (125 µg/L).

One of the spiked seawater sample was processed and the recoveries of the analytes were calculated as the peak area ratios in the spiked samples to those of standard solutions containing the same concentration of the analytes. Bifenox was not included in the study for the reason mentioned above. The results obtained are presented in Table 5.

Table 5. Recoveries obtained for real a seawater sample spiked with the target herbicides (*n* = 3).

Compound [1]/EF	Recovery (%)
Iodosulfuron-methyl-sodium	100 ± 2
Tritosulfuron	143 ± 3
Tribenuron-methyl	109 ± 4
Metribuzin	84 ± 4
Triflusulfuron-methyl	115 ± 6
Irgarol	100 ± 9
Cypermethrin	106 ± 6

[1] Established for a concentrations of 25 µg/L for metribuzin and irgarol, 125 µg/L for cypermethrin and 200 µg/L for the rest of compounds.

The extraction recoveries listed in Table 5 indicate that the performance of the SiO_2 NPs reinforced TEOS-MTEOS capillary for this kind of samples is similar to that of standard solutions. It has to be remarked that the real samples were processed without adjusting pH or the ionic strength. The results of the above table indicate that those parameters had a negligible influence on the method performance in this kind of samples. The same capillary was used throughout the study with the real samples (more than 30 runs). Thus, the stability can be considered satisfactory.

Finally, the proposed method was applied to process the extract obtained from a soil spiked with metribuzin, irgarol and bifenox (at a concentration of 25 ng/g each) and cypermethrin (40 ng/g).

For extraction of the target analytes, ultrasonic assisted extraction with methanol was used (see Section 2.5 for details). As an illustrative example, in Figure 4 are depicted the chromatograms obtained for soil sample and the same spiked with the analytes. Although the chromatographic profiles were suitable, the recoveries of the analytes were lower than those obtained for water samples (<65%).
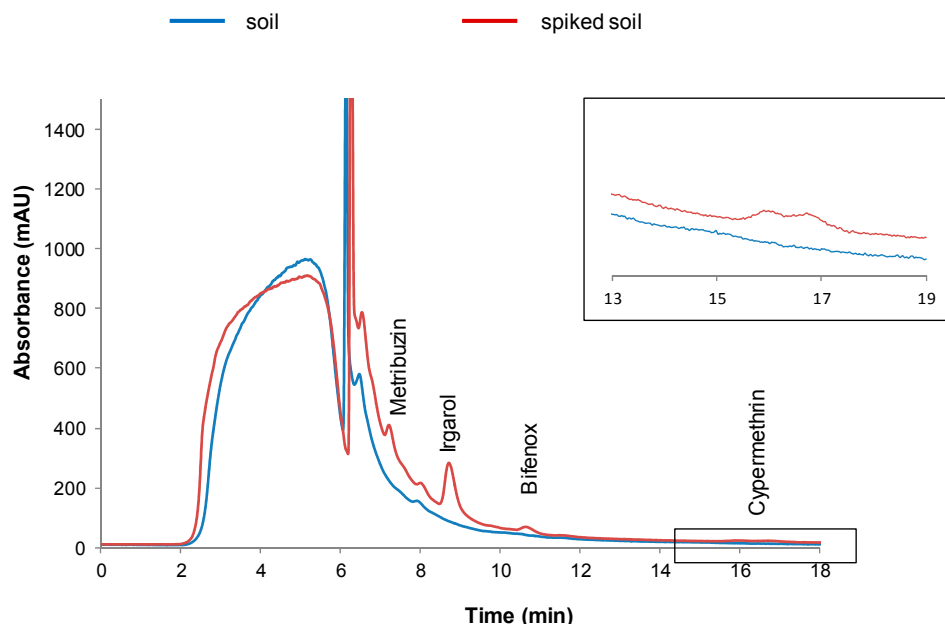

Figure 4. Chromatograms obtained under the proposed conditions for the extract obtained from a soil sample and the same sample spiked with metribuzin, irgarol, bifenox (25 ng/g), and cypermethrin (40 ng/g).

4. Discussion

To date, IT-SPME has been applied to organic pollutants mainly using non-polar capillary coatings, especially PDMS-based coatings; PEG coatings have also been used in some applications [2,3]. The results of this study show that PEG modified with FFAP may improve the extraction efficiency of high polar herbicides, although little improvement with respect to PDMS-based coatings was found for most of the tested analytes. On the other hand, a TEOS-MTEOS coating reinforced with SiO_2 NPs provided the highest enrichment factors for all the tested herbicides. Therefore, this phase can be considered a valid alternative for the extraction of a broad group of pollutants, including highly polar compounds, which are particularly difficult to isolate from aqueous matrices with commercially available extractive capillary columns. The presence of the SiO_2 NPs is essential for interaction with the most polar compounds. These NPs are also more effective than other type of NPs such as carbon nanotubes [12,13].

The proposed SiO_2 NPs modified TEOS-MTEOS coating offers suitable analytical performance for aqueous solutions of the analytes, and good selectivity for sea and transition water samples. Preliminary experiments with soil extracts have shown that the proposed extractive capillary could be used for this kind of samples too, although a purification of the extract obtained before loading it into the IT-SPME may be required to improve the extraction effectiveness.

5. Conclusions

In this study we have evaluated and compared the extraction efficiency of different sorbents for the extraction of a wide variety of herbicides by IT-SPME. Capillary columns commercialized with PDMS-, PEG- based coatings, and synthesized TEOS-MTEOS and SiO_2 NPs modified TEOS-MTEOS coatings have been assayed. The results obtained demonstrated that a TEOS-MTEOS coating reinforced with

SiO$_2$ NPs is the best option for the extraction of the herbicides included in the study, particularly for the most polar compounds. This can be explained by the fact that the presence of free –OH groups in the surface of SiO$_2$ NPs facilitates the interaction with the functional groups of the analytes. Thus, the extraction is the result of the combination of hydrophobic interactions with the polymeric network and hydrogen bonding and dipole-dipole interactions with free –OH of the SiO$_2$ NPs. The reliability of the proposed conditions has been tested by analyzing environmental waters and soil extracts.

Author Contributions: C.E.R.-P. performed part of the experiments; the rest of authors designed and performed part of the experiments, analyzed the data and wrote the paper.

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