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Use of green coating (cork) in solid-phase microextraction for the determination of organochlorine pesticides in water by gas chromatography-electron capture detection

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ABSTRACT

A novel method for the determination of organochlorine pesticides in water samples with extraction using cork fiber and analysis by gas chromatography with electron capture detector was developed. Also, the procedure to extract these pesticides with DVB/Car/PDMS fiber was optimized. The optimization of the variables involved in the extraction of organochlorine pesticides using the aforementioned fibers was carried out by multivariate design. The optimum extraction conditions were sample temperature 75 °C, extraction time 60 min and sodium chloride concentration 10% for the cork fiber and sample temperature 50 °C and extraction time 60 min (without salt) for the DVB/Car/PDMS fiber. The quantification limits for the two fibers varied between 1.0 and 10.0 ng L^{-1}. The linear correlation coefficients were >0.98 for both fibers. The method applied with the use of the cork fiber provided recovery values between 60.3 and 112.7 and RSD ≤ 25.5 ($n=3$). The extraction efficiency values for the cork and DVB/Car/PDMS fibers were similar. The results show that cork is a promising alternative as a coating for SPME.

1. Introduction

During the period of around 1950 to 1970 organochlorine pesticides (OCPs) were widely used to combat agricultural pests and to control diseases vectors [1,2]. OCPs, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are classified as persistent organic pollutants (POPs) [3]. Humans and other animals exposed to POPs can develop various health problems including cancer, genetic variation and diseases of the immune system. OCPs are characterized by their low water solubility and high lipid solubility and thus they easily accumulate in the environment and in living organisms. This results in biomagnification through the food chain. Nowadays, these compounds are forbidden around the world, but due to their physicochemical properties they can still be found at trace levels in the environment [2].

In the determination of OCPs a sample preparation step is required prior to analysis [4,5]. This is the most time consuming step in the analytical procedure and is an important factor regarding the success of the chemical analysis [6]. Initially, classical techniques of sample preparation, such as soxhlet and liquid–liquid extraction, that employed large amounts of toxic organic solvents were used. However, since the 1980s research on sample preparation techniques has been focused on the importance of the use of small amounts of sample and organic solvents. Over time, analytical chemists have developed environmentally friendly methods with few steps, eliminating the use of toxic reagents and reducing or eliminating the use of organic solvents. In this scenario, a notable procedure is solid-phase microextraction (SPME), a solvent-free sample preparation technique which combines sampling, isolation and enrichment in a single step. SPME was developed by Pawliszyn and Artur in the late 1980s and early 1990s and since then it has been adapted for use in a number of applications involving different types of analysis [7]. In addition, new coatings for SPME fibers are developed continuously and currently biosorbent and Fe_3O_4-coated bamboo charcoal were proposed [8–12].

Cork is a biosorbent and, being a natural material, it is renewable and biodegradable. In this study, its use as an extractor phase in SPME was investigated. Cork was chosen due to its sorption capacity and because the number of publications in indexed journals related to the application of this material is increasing, reflecting the growing interest of the scientific community in research on cork [13]. The sorption potential of cork for the removal of some pollutants, such as PAHs, bifenthrin, alpha-cypermethrin, acetaminophen and chrysoidine, from aqueous solutions has been evaluated [14–18]. The use of cork as a new (green) coating for SPME was introduced by our group and initially the new fiber was employed for the determination of PAHs in river

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water samples [11]. Continuing our studies along this line, the use of cork fiber is proposed for the extraction of OCPs in water samples followed by determination by gas chromatography with electron capture detection. The cork employed as a raw material for SPME fibers was obtained from wine bottle stoppers. Thus, this extractor phase is easily obtained from a natural, renewable and biodegradable source.

2. Experimental

2.1. Reagents and solutions

Stock solution of eight analytes, α-BHC, heptachlor, aldrin, heptachlor epoxide, endrim, β-endosulfan 4,4′D,D,D and endrin aldehyde, in hexane:toluene (50:50) was obtained from Supelco (Bellefonte, USA) at a concentration of 25 μg mL^{-1}. From this solution, diluted solutions were prepared in hexane (Sigma-aldrich, St. Louis, USA) for optimization and validation of the method. Sodium chloride (Vetec, Rio de Janeiro, Brazil) was used to adjust the ionic strength.

2.2. General materials and instrumentation

The cork fiber was prepared using araldite (10-min) epoxy glue (Brascola, São Bernardo do Campo, Brazil), a heating block (Dist, Florianópolis, Brazil) and Waterproof 15 (Carborundum, Rio de Janeiro, Brazil). Two commercial fibers (PDMS, 100 μm and DVB/Car/PDMS, 50/30 μm) were tested.

A thermostatic bath (Lab Companion RW 0525G, Seoul, South Korea) and a magnetic stirrer were used for the direct immersion (DI)-SPME extraction. An ultrasonic bath (Unique, São Paulo, Brazil) and laboratory oven (Fanem 515B, São Paulo, Brazil) were used for the cleaning of the cork.

2.3. Instrumentation and chromatographic conditions

The optimization of the method employing the cork fiber was carried out using a Shimadzu GC–MS QP2010 Plus gas chromatograph, equipped with a Zebron ZB-5MS (5% diphenyl-95% dimethylpolysiloxane) capillary column (30 m × 0.25 mm × 0.25 μm), split/splitless injector and mass spectrometer detector. The optimization for the DVB/CAR/PDMS fiber and validation of the methods for the two fibers (commercial fiber and cork) were carried out using a Shimadzu GC-14B gas chromatograph equipped with an electron capture detector (ECD). The column oven temperature program and injection conditions for the GC-ECD were similar to those used for the GC–MS and the ECD temperature was 280 °C.

The conditions applied for the GC–MS were helium as the carrier gas at a flow rate of 0.83 mL min^{-1}. The column oven temperature program was 100 °C (1 min) followed by ramping at 10 °C min^{-1} to 180 °C and then 3 °C min^{-1} to 260 °C. The injection was performed in the splitless mode, the injector temperature was 260 °C and the DI-SPME desorption time was 7 min. The mass spectrometer was operated in the electron impact (EI) ion source mode at 70 eV. The transfer line and the ion source temperatures were set at 280 °C and 250 °C, respectively. The solvent cut time was 10 min.

2.4. Experimental procedure

2.4.1. Optimization of the commercial fiber

The best commercial fiber was selected by spiking 15-mL aqueous samples with 100 ng L^{-1} of each target compound. SPME vials (22 mL) obtained from Supelco were used in this study. The fibers were immersed in the sample for 60 min at 60 °C and agitated with a magnetic stirring at 1000 rpm. After the extraction the analysis was carried out by GC-ECD.

2.4.2. Preparation of the cork fiber

The cork stoppers of wine bottles were placed in vials with ultra-pure water and left for 2 h in an ultrasonic bath. This procedure was repeated until the ultra-pure water remained clean. The cork stoppers were then kept in an oven set at 110 °C for 12 h. Their performance of extraction can be similar regardless of the source of cork. The composition of cork is mainly suberin (40%) and lignin (24%), and polysaccharides (20%) (cellulose and hemicellulose), which have a hydrophilic character, along with waxes and other extractives (15%). Small differences in the composition of the cork are not significant. Furthermore during conditioning of the cork fiber at 260 °C there is partial decomposition of cork and small differences in composition are eliminated.

The fiber material was prepared according to method used in our previous study [17]. The cork powder (200 mesh) was immobilized with epoxy glue on wires of NiTi with 2 cm length and 0.2 mm thickness. The fiber samples were then placed on a heating block and exposed to a temperature of 180 °C for 90 min. The cork fiber samples produced were conditioned at 260 °C for 60 min in a GC injection port.

2.4.3. Optimization of DI-SPME procedure for determination of OCPs in water samples

A central composite design, totalizing 17 experiments, was used to optimize the extraction parameters and the experimental data were processed using the *Statsoft Statistica 8.0* computer program. The response used as the input data was obtained by calculating the geometric mean of the set of 8 normalized peak areas corresponding to the analytes. In the *Statsoft Statistica* program the desirability function was used.

Pesticide concentrations of 10 μg L^{-1} (cork fiber and GC–MS) and 0.1 μg L^{-1} (DVB/CAR/PDMS fiber and GC-ECD) were used for this step. The variables extraction temperature (20–80 °C), extraction time (30–120 min) and sodium chloride concentration (0–35% m/v) were simultaneously optimized.

2.4.4. Optimized sample preparation for cork fiber and for DVB/CAR/PDMS commercial fiber

In the procedure carried out with cork fiber, 15 mL of the sample solutions with 10% of sodium chloride concentration were transferred to vials (22 mL, Supelco) and equilibrated before the extraction step. The fiber was immersed in the sample for 60 min at 75 °C and agitated with a magnetic stirring at 1000 rpm. After this period, the fiber was immediately inserted into the GC injector for desorption at 260 °C for 7 min. The optimized procedure with DVB/CAR/PDMS was similar, but without salt addition and with an extraction temperature of 50 °C.

2.4.5. Evaluation of the methods developed with cork fiber and DVB/Car/PDMS fiber

The detection and quantification limits, linear range and linear correlation coefficient (r) were the figures of merit used to evaluate the methods developed with cork fiber and DVB/Car/PDMS fiber.

2.4.6. Accuracy and precision tests and application of the method developed with cork fiber

The method precision and accuracy were studied by spiking mineral water samples (Serra Catarinense, Angelina, Santa Catarina, Brazil) at different concentration levels.

The method developed with the cork fiber was used to determine pesticide concentrations in river water samples collected from

the Camboriú river, in the city of Balneário Camboriú, Santa Catarina State, Brazil. The samples were stored in glass bottles, properly sealed and stored in a refrigerator at 4 °C until analysis.

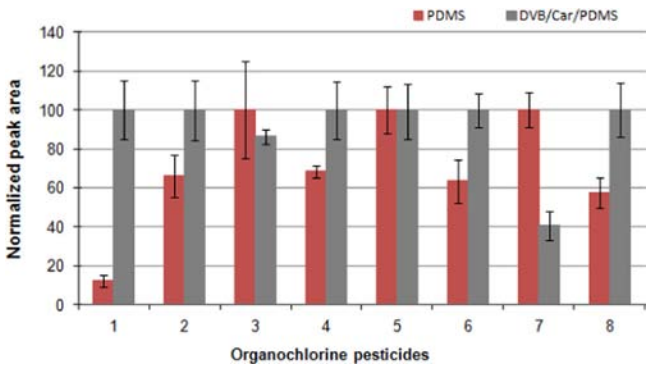

Fig. 1. Comparison of the commercial fibers PDMS and DVB/Car/PDMS in the extraction of organochlorine pesticides by DI-SPME. Analytes: (1) α-BHC, (2) heptachlor, (3) aldrin, (4) heptachlor epoxide, (5) endrin, (6) β-endosulfan, (7) 4,4′D,D,D, and (8) endrin aldehyde.

3. Results and discussion

3.1. Optimization of commercial fiber

In general, the two commercial fiber samples showed good extraction efficiency (Fig. 1). The DVB/Car/PDMS was selected to continue this study because it presented better performance for the extraction of α-BHC. Also, other authors in the literature describe the DVB/Car/PDMS as the best fiber for the analysis of OCPs [19–21].

3.2. Optimization of DI-SPME extraction conditions

The analytes were extracted by DI-SPME. The optimum results for the cork fiber were obtained with an extraction time of 60 min at 75 °C and sodium chloride concentration of 10% (m/v) (Fig. 2). In the case of the DVB/Car/PDMS fiber, the best efficiency was obtained using an extraction of 60 min at 50 °C without the addition of salt (Fig. 3). Both fiber SPME coatings extracted the analytes by adsorption. The cork fiber possesses polar groups such as hydroxyl, carboxyl and alkoxide, while these groups are not present in the DVB/Car/PDMS fiber [11]. The OCPs determined in this study have

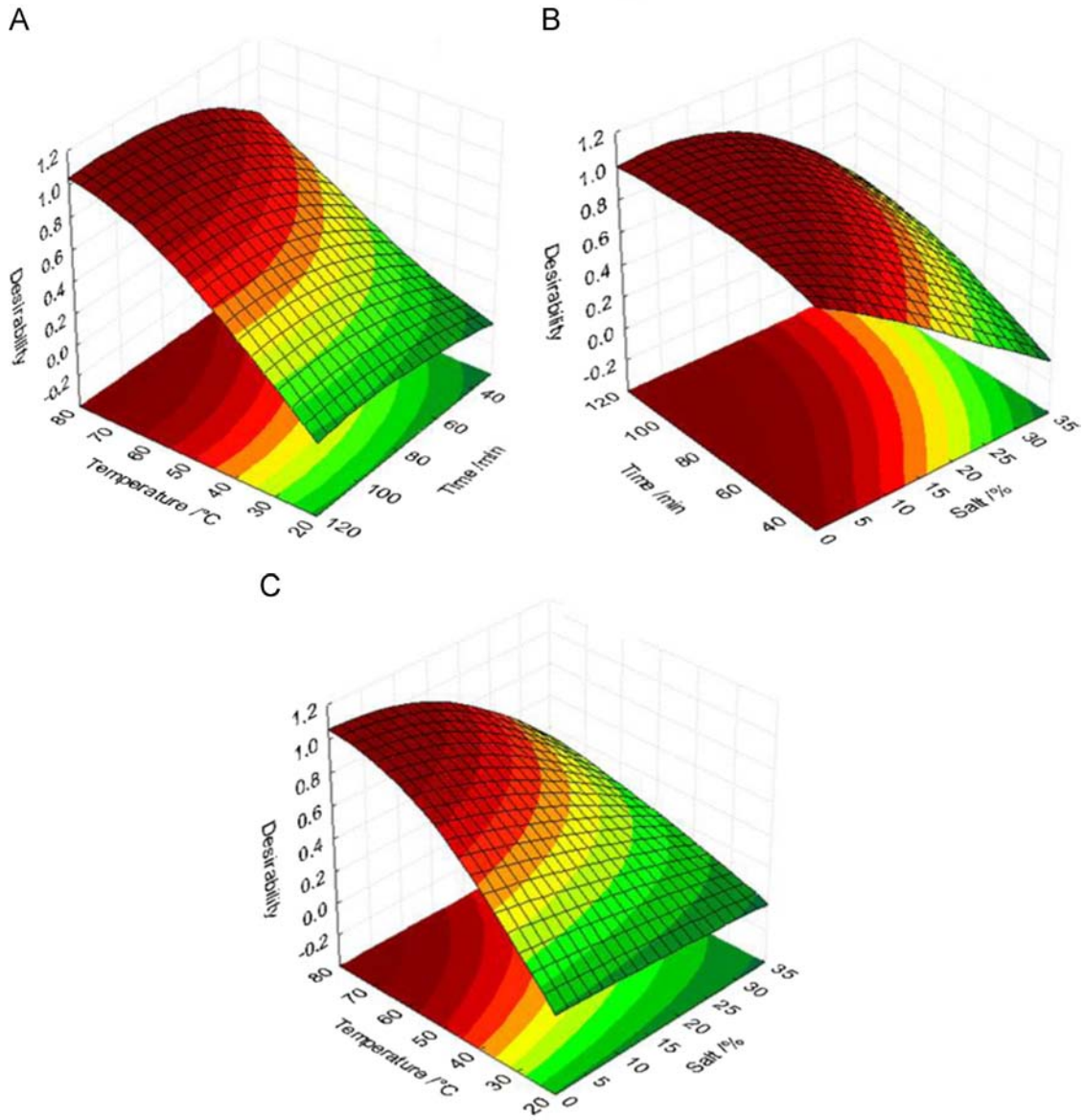

Fig. 2. Response surface: (A) temperature versus time, (B) time versus salt and (C) temperature versus salt obtained in the extraction of analytes by DI-SPME with cork fiber.

low solubility in water and thus these analytes are expected to partition more readily toward the fiber coating with less polar groups, that is, DVB/Car/PDMS. Hence, the optimum extraction temperature for the cork fiber is higher than that for the DVB/Car/PDMS. The higher temperature favors the diffusion of the analytes toward the cork fiber. The analyte response for the DVB/Car/PDMS fiber decreased with the addition of salt. The experiments with the cork fiber showed good extraction results up to a salt concentration of 10% and above this level the extraction efficiency decreased. The study on the salting-out effect considered the features of the analyte, sample and extractor phase. In general, the compounds studied have low solubility in water; therefore samples with high ionic strength do not improve the extraction [11]. The good results obtained with a salt concentration of 10% for the cork fiber can be explained by the presence of polar groups in the coating. The optimum salt concentration of 10% was used in the method employing the cork fiber, although in the case of α-BHC better extraction efficiency was obtained with a salt concentration higher than 10% (response surfaces not showed). However, according to the data in Table 1, α-BHC is more soluble in water than the other analytes and thus the salt addition favors the diffusion of the α-BHC toward the cork fiber.

3.3. Comparison of the methods employing cork fiber and DVB/Car/PDMS fiber

The extraction efficiency of the cork fiber was similar to that of the DVB/Car/PDMS fiber and both provided good correlation coefficients (Tables 2 and 3).

Table 1
Water solubility of the target organochlorine pesticides.

Compound	Solubility in water[a] (mg L^{-1})
α-BHC	1.63
Heptachlor	0.056
Aldrin	0.01–0.02
Heptachlor epoxide	0.35
Endrin	0.23
B-Endosulfan	0.33
4,4′D,D,D	n/a
Endrin aldehyde	n/a

[a] Values taken from Ref. [20]; (n/a) data not available.

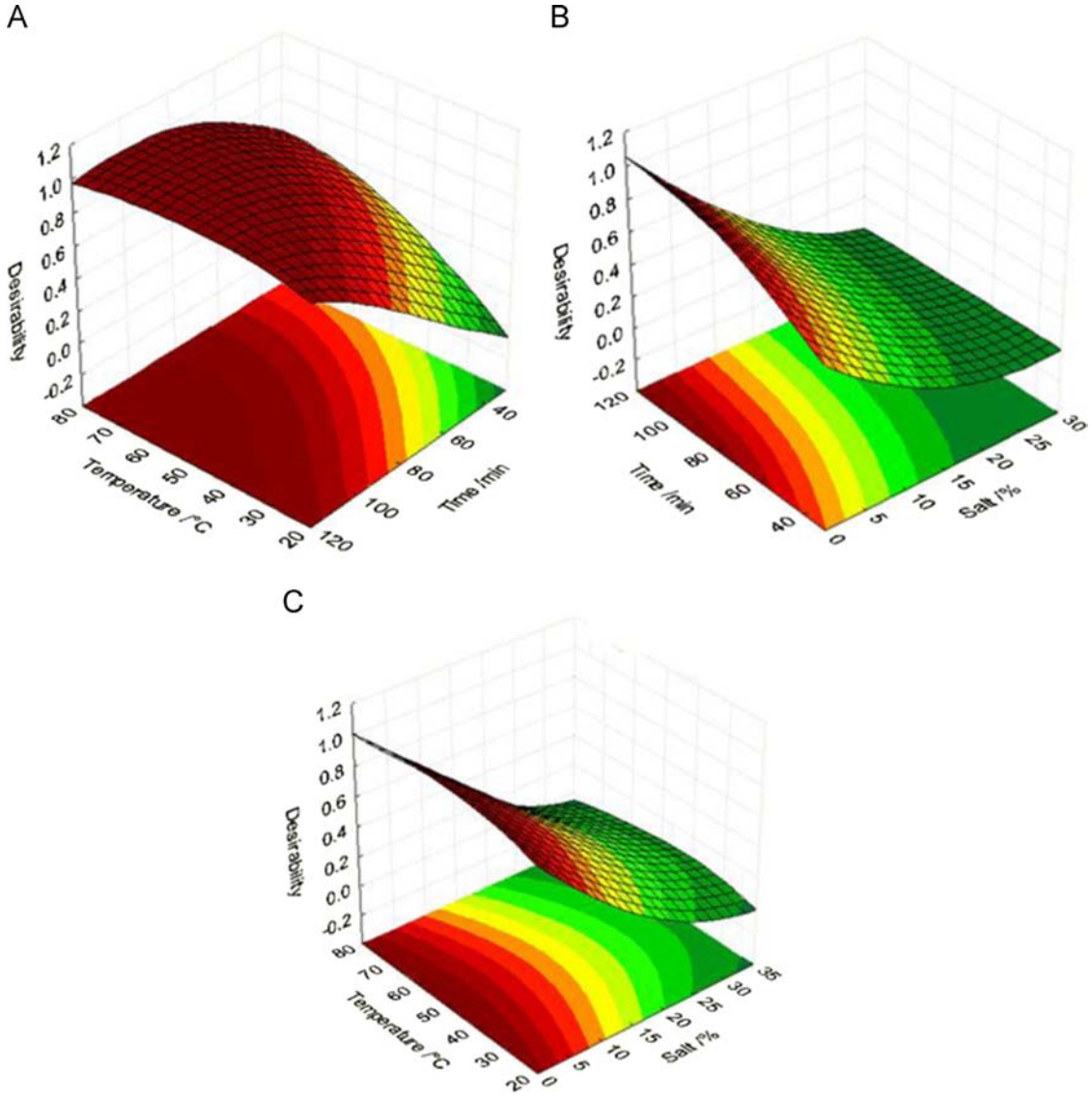

Fig. 3. Response surface: (A) temperature versus time, (B) time versus salt, and (C) temperature versus salt obtained in the extraction of analytes by DI-SPME with DVB/Car/PDMS fiber.

Table 2
Linear range, correlation coefficients and detection and quantification limits obtained for the proposed method for the determination of pesticides in river water samples using cork fiber.

Compound	LOD (ng L^{-1})	LOQ (ng L^{-1})	Linear range (ng L^{-1})	Analytical curve	*r*
α-BHC	3.0	10.0	10.0–75.0	$y=15035.97945x-72792.12172$	0.9891
Heptachlor	0.8	2.5	2.5–50.0	$y=206.77733x+7787.48267$	0.9995
Aldrin	0.3	1.0	1.0–50.0	$y=16085.19267x-60746.764$	0.9973
Heptachlor epoxide	0.3	1.0	1.0–50.0	$y=54297.79458x-53894.6614$	0.9968
Endrin	0.3	1.0	1.0–50.0	$y=39928.1012x-26536.74191$	0.9996
B-endosulfan	0.8	2.5	2.5–50.0	$y=30576.58398x+5699.99636$	0.9986
4,4′D,D,D	0.8	2.5	2.5–50.0	$y=24489.19191x-24776.85032$	0.9978
Endrin aldehyde	3.0	10.0	10.0–75.0	$y=13926.99023x-107385.7777$	0.9835

Table 3
Linear range, correlation coefficients, detection and quantification limits obtained for the proposed method for the determination of pesticides in river water samples using DVB/Car/PDMS.

Compound	LOD (ng L^{-1})	LOQ (ng L^{-1})	Linear range (ng L^{-1})	Analytical curve	*r*
α-BHC	0.3	1.0	1.0–50.0	$y=20939.55592x-6575.20826$	0.9983
Heptachlor	0.8	2.5	2.5–50.0	$y=8351.65899x+17780.93354$	0.9942
Aldrin	0.8	2.5	2.5–50.0	$y=15292,95x-11375.53165$	0.9935
Heptachlor epoxide	0.3	1.0	1.0–50.0	$y=26272.68416x-9575.66606$	0.9999
Endrin	0.3	1.0	1.0–50.0	$y=23459.42115x+7963.08211$	0.9999
B-Endossulfan	0.8	2.5	2.5–50.0	$y=13531.6x+23646.56667$	0.9843
4,4′D,D,D	3.0	10.0	10.0–100.0	$y=8589.33171x-65907.54878$	0.9833
Endrin aldehyde	3.0	10.0	10.0–100.0	$y=52050.04404x-50625.66198$	0.9791

Table 4
Recoveries tests (%) and precision (RSD %) using the proposed SPME method with cork fiber.

Compound	Spike level (ng L^{-1})	Repeatability		Intermediate precision	
		R (%)	RSD (%)	*R* (%)	RSD (%)
α-BHC	10.0	102.7	10.9		
Heptachlor	2.5	111.3	0.5		
	5.0	60.3	19.2	87.0	12.0
	10.0	88.4	17.1		
Aldrin	1.0	103.2	17.3	–	–
	2.5	100.8	2.2	–	–
	5.0	103.9	17.3	85.1	7.8
	10.0	100.6	16.1		
Heptachlor epoxide	1.0	102.7	10.4	–	–
	2.5	106.9	5.8	–	–
	5.0	88.7	19.2	73.6	20.0
	10.0	83.2	18.0		
Endrin	1.0	80.4	14.6	–	–
	2.5	96.5	8.3	–	–
	5.0	87.6	8.3	94.8	3.3
	10.0	96.6	0.5		
B-Endosulfan	2.5	67.7	5.8	–	–
	5.0	112.7	17.0	69.4	1.0
	10.0	104.5	25.5		
4,4′D,D,D	2.5	96.0	17.8	–	–
	5.0	74.9	11.9	81.6	6.6
	10.0	91.4	9.1		
Endrin aldehyde	10.0	103.0	7.5		

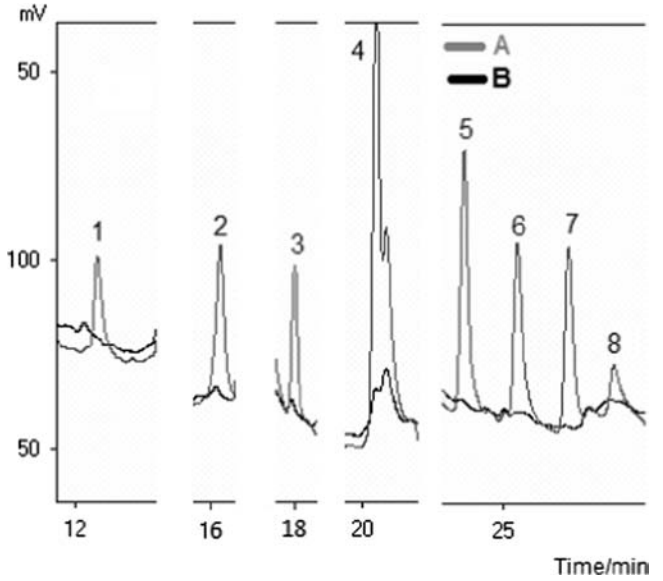

Fig. 4. Chromatograms obtained after extraction by DI-SPME with cork fiber and determination by GC-ECD, (A) river water sample spiked at 25 ng L^{-1} (B) river water sample from Camboriú River not spiked. Analytes: (1) α-BHC, (2) heptachlor, (3) aldrin, (4) heptachlor epoxide, (5) endrin, (6) β-endosulfan, (7) 4,4′D,D,D, and (8) endrin aldehy.

The limits of quantification (LOQ) obtained for the two fibers for heptachlor, heptachlor epoxide, endrin, β-endosulfan and endrin aldehyde were the same, while the LOQ obtained for 4,4′D,D,D and aldrin were lower for the cork fiber. However, the commercial fiber provided a lower LOQ than the cork fiber for α-BHC.

The extraction efficiency of the cork fiber can be explained by dipole–dipole interactions occurring with all analytes. Moreover, the cork fiber extracts compounds with double bonds through π–π interactions and it interacts with compounds containing oxygen atoms via hydrogen bonding.

3.4. Accuracy and precision studies and analysis of real samples with cork fiber

The optimum results for accuracy and precision were obtained with the method developed using the cork fiber (Table 4). The

recovery tests and RSD varied from 60.3 to 112.7% and 0.5 to 25.5, respectively. Furthermore, the cork fiber presented similar performance of extraction for at least 50 extractions. Fig. 4 shows the chromatograms obtained for non-spiked river water samples and for those spiked with OCPs using extraction by DI-SPME and with cork fiber. In the river water sample analyzed the target compounds were not detected.

4. Conclusions

It was once again verified in this study that cork fiber has potential as a coating for SPME. Furthermore, the wine bottle stoppers used as the raw material are easy to obtain. The method developed with cork fiber showed quantification limits similar to those obtained when the procedure is carried out with DVB/Car/PDMS. The cork fiber was successfully applied in the analysis of OCPs at ultra-trace levels in water samples and it represents a promising green coating for SPME.

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