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% dimethyl-polysiloxane) 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 hemi-cellulose), 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