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A high throughput approach to rotating-disk sorptive extraction (RDSE) using laminar cork for the simultaneous determination of multiclass organic micro-pollutants in aqueous sample by GC-MS

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ABSTRACT

In this study, a high throughput approach to rotating-disk sorptive extraction (RDSE) using laminar cork as extraction phase is demonstrated for the first time in the determination of 20 multiclass organic micro-pollutants including pesticides, PAHs and UV filters compounds from aqueous samples with gas chromatography mass spectrometry (GC-MS). The influencing parameters (desorption solvent, volume and time, extraction time and sample pH and ionic strength) were carefully optimized using multivariate designs. The optimal conditions were 10 min for extraction using 35 mL of water samples and a liquid desorption using 1 mL of MeOH:AcOEt (50:50% v/v) for 20 min. A low-cost apparatus that allows six extractions simultaneously, providing a high throughput of 5 min per sample turnaround times, considering the sample preparation step was used for the first time in this modified RDSE methodology. Satisfactory analytical performance was achieved with limits of detection (LOD) between 0.08 and 1.5 μg L^{-1} and limits of quantification (LOQ) between 0.3 and 4.8 μg L^{-1}. The relative recoveries for the analytes were determined using river and lake water samples spiked at different concentrations and ranging from 80% to 119% for all analytes, with relative standard deviations (RSD) lower than 20%. The extraction efficiency obtained for the proposed configuration with laminar cork was significantly superior to powdered cork, demonstrating an interesting new configuration for new applications.

1. Introduction

The world's population has grown dramatically in recent decades, along with increasing globalization and faster economic progress. With the increase in population there is a need to improve industrial and agricultural processes in order to meet demand. This industrial and technological progress causes environmental impacts in two main ways: resource consumption and waste generation [1]. Therefore, wastes from the diffuse sources of pesticides used in agriculture, industrial wastewater effluent, and municipal wastewater are daily generated in tons as a source of contamination for soils, water and atmospheric air [2,3].

The organic micro-pollutants (OMPs) have become a worldwide issue of increasing environmental concern. OMP is an operational definition for a group of compounds including more than 20 classes, which are not covered by existing water quality regulations due to their trace concentrations (i.e., ng L^{-1} to a few μg L^{-1}). Their occurrence does not only raise toxicological concerns in the environmental ecosystems, but also represents threats to public health if present in drinking water, since they can cause adverse effects on living organisms, such as antibiotic resistance genes, endocrine disrupting effects and mutagenesis [4,5].

Examples of organic contaminants which have been widely reported in different matrices include pharmaceutically active compounds, personal care products such as UV organic filters, products derived from the incomplete burning of fossil fuels like polycyclic aromatic hydrocarbons and BTEX, trihalomethanes, pesticides, including their transformation products [6].

The determination of OMPs from environmental aquatic media is a matter of increasing concern nowadays. Hence, there is a growing need to develop reliable analytical methodologies capable of extracting

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different classes of analytes with high sensitivity and selectivity [7].

Considering their low concentration in aqueous samples, a sample preparation step is a key factor in determining OMPs [8]. Therefore, extraction techniques are mainly used to achieve one or more of these objectives: 1) separation of analytes from potentially interfering compounds present in the matrix, 2) preconcentration of the analytes in order to improve the limits of detection and quantification and 3) adequacy of the sample to the analytical instrument [9].

Numerous analytical methodologies have been used as extraction techniques for the determination of OMPs in aqueous samples, including the following: magnetic solid phase extraction (MSPE) [10], solid phase extraction (SPE) [11], dispersive liquid– liquid microextraction (DLLME) [12], stir-bar sorptive extraction (SBSE) [13] and solid phase microextraction (SPME) [14].

Rotating disk sorptive extraction (RDSE) is an integrated extraction/stirring technique, proposed in 2009 by Richter and co-workers, which has been used for the extraction/preconcentration of various organic micro-pollutants from aqueous samples [15]. Its general principles are based on SPME and SBSE and consist of two fundamental steps: extraction of the analytes from the sample to an extraction phase, followed by the desorption of the analytes to a small volume of a suitable solvent [7].

This technique has been successfully applied for the determination of parabens in water samples [16], pesticides in water using the commercial phases Oasis® HLB and polydimethylsiloxane (PDMS) [17], pharmaceuticals and hormones in water [18], as well as a comparison between biosorbents (cork powder and montmorillonite) and the commercial sorbent octadecyl silane-C18 demonstrating better performance for biosorbent cork powder [19].

The disk cavity provides high versatility for RDSE-based methodologies, allowing the employment of commercial or alternative materials as sorbent phases both in laminar and powder form. Furthermore, RDSE is an attractive approach since it requires low analyst supervision, reduced consumption of organic solvents and green technology promotion [17]. However, in order to achieve good analytical performance, this technique requires a solvent drying apparatus. Due to the large amount of solvent required to cover the disk height for the desorption, high dilution of the extract and consequently a significant loss of the analytical signal is observed if no drying step is adopted [20]. For this reason, proposing high throughput RDSE modifications which reduce the consumption of solvent and eliminate the drying step are of great interest [7].

Our research group introduced a low-cost lab-made setup to promote the extraction of multiple samples simultaneously [9]. The analysis throughput can be considerably increased with this experimental setup, because this configuration allows the magnetic stirrers to remain at the same stirring rate, and various samples can be extracted at the same time. Alongside this, improvements and modifications of the microextraction techniques using green sorptive phases which allow good analytical performances are of great interest for research.

In this regard, this paper reports a high throughput approach to the RDSE technique, using for the first time the lab-made setup for coupling up to six magnetic stirrers in a modified RDSE using laminar sorbent technique and efficiently performing the extraction of 20 multiclass organic micro-pollutants (ethylbenzene, o-Xylene, acenaphthylene, fluorene, trifluralin, phenanthrene, anthracene, pendimethalin, 2-ethylhexyl-p-dimethylaminobenzoate (EHPABA), pyrene, 3-(4-methylbenzylidene)camphor (MBC), benzo[a]anthracene, chrysene, permethrin, benz(e)acephenanthrylene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno [1,2,3-cd]pyren and benzo[ghi]perylene) from aqueous samples with separation/detection by GC-MS. Very few studies using many analytes for RDSE can be found in the literature, and according to our knowledge, a high throughput approach to this technique has not previously been explored.

2. Experimental

2.1. Materials and reagents

Analytical standards of 20 analytes (ethylbenzene, o-xylene, acenaphthylene, fluorene, trifluralin, phenanthrene, anthracene, pendimethalin, 2-ethylhexyl-p-dimethylaminobenzoate (EHPABA), pyrene, 3-(4-methylbenzylidene)camphor (MBC), benzo[a]anthracene, chrysene, permethrin, benz(e)acephenanthrylene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno [1,2,3-cd]pyren and benzo[ghi]perylene) were purchased from Sigma-Aldrich (Milwaukee, WI, USA) and they were used to prepare single stock solutions of 100 mg L^{-1} in methanol obtained from Merck (Rio de Janeiro, RJ, Brazil). After the individual preparation, a working solution containing all the analytes at a concentration of 10 mg L^{-1} was performed in methanol. The buffer solutions - citric acid and sodium phosphate dibasic - used for the pH adjustment were purchased from Vetec (Rio de Janeiro, Brazil). Sodium chloride obtained at Synth (São Paulo, Brazil) was used for the salting-out effect studies. High-performance liquid chromatography (HPLC) grade ethyl acetate (AcOEt) and acetone (AC) were purchased from Merck (Kenilworth, NJ, USA). Additionally, ultrapure water (18.2 MΩ cm) was purified by the Mega Purity water purification system (Billerica, MA, USA).

For the extractions, six magnetic stirrers (Fisatom, SP, Brazil) were connected to a Variac Tension Regulator TDGC2-1 1KVA/4 AMP (EXA Instruments, SP, Brazil) by power strip (NBR 20605, Power Line). A Digital Multimeter ET-1002 (Minipa, SP. Brazil) was used to control the voltage of the magnetic stirrers according to a previous study by our group [9]. The extractions were performed in 40-mL capacity vials.

2.2. Instrumental conditions

A Shimadzu GC-MS QP2010 Plus gas chromatograph, equipped with a split/splitless injector and mass spectrometer detector (Kyoto, Japan), with a Zebron ZB-5MS capillary column (30 m × 0.25 mm × 0.25 µm; Torrance, CA, USA) was used for the chromatographic analysis. The liquid injection was performed in splitless mode, with the injector temperature set at 250 °C. The initial oven temperature was 40 °C (5 min), which subsequently increased at 20 °C min^{-1} to 80 °C and, a second time, increased at 6 °C min^{-1} to 300 °C (10 min). Helium was used as the carrier gas at a flow rate of 1.0 mL/min. For the GC-MS, the transfer line and the ion source temperatures were set at 280 and 250 °C, respectively. The mass spectrometer was operated in electron impact ionization (EI) mode at 70 eV. The multiresidue analytes were determined in selected ion monitoring (SIM) mode and the mass/charge (m/z) ratios employed are shown in Table S-1 of the Supporting Information. The m/z values in bold were used for the quantitative determination of the analytes.

2.3. Preparation and characterization of the biosorbent material

Briefly, cork stoppers were conditioned in a beaker containing ultrapure water for 2 h under ultrasonic agitation. This procedure was repeated until colorless water was obtained, indicating that the cork stoppers were clean. Then, cork stoppers were left in an oven at 110 °C for 12 h. After cleaning the cork stopper, a slicer was used to cut the cork stoppers in the form of sheets with approximately the same thickness (2 mm). A circular drill with a diameter of 10 mm was used to fragment the material into disks, and these were kept in an ultrasonic bath with chloroform for 30 min followed by 10 min with water. At the end of the process, with the material already dry, all the circular sheets were weighed, thus guaranteeing the same amount of sorbent in all extractions (0.03 g).

The characterization of the laminar cork was performed using an

ABB FTLA 2000 Attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR) (Zurich, Switzerland). A PerkinElmer 2400 CHNS/O analyzer was used to perform elemental analysis. Thermogravimetric analysis was performed in a Shimadzu thermogravimetric analyzer model TGA-50 (Tokyo, Japan) under heating rate of 10 °C min^{-1} to 600 °C, N_2 atmosphere and flow rate of 50 mL/min in a platinum cell. A Hitachi TM 3030 (Tarrytown, NY, USA) scanning electron microscope (SEM) was used to evaluate the morphology of the material.

2.4. Modified RDSE apparatus containing the laminar cork

The modified RDSE proposed in this study consists of the rotating disk containing the circular laminar cork (10 mm of diameter) placed inside the disk cavity. As the laminar cork and the disk cavity have the same diameter, it was not necessary to use any type of glue to make the material adhere, nor use of the Teflon cap. This new configuration, which is reduced in size by approximately 15%, allowed lower amounts of solvent to proceed to the desorption step in comparison to the traditional RDSE apparatus, besides permitting the use of larger amounts of extractive phase. Magnetic stirrers connected to a voltage regulator allowed simultaneous extractions to increase the method throughput. A scheme comparing the new configuration used in this study and the traditional configuration is shown in Fig. 1.

2.5. Optimization of the RDSE procedure

The experimental parameters that can influence the extraction and the liquid desorption of the target compounds were evaluated as described below. Throughout the optimization, geometric means of the normalized peak areas corresponding to the compounds studied were used to plot the graphics.

Liquid desorption: desorption solvents were investigated based on a simplex-lattice design, containing 12 experiments (including a triplicate at the central point), using methanol (MeOH), ethyl acetate (AcOEt) and acetone (AC) to obtain a triangular surface from the experimental strategy. After that, the desorption time and volume required for the liquid desorption were investigated applying a Doehlert design, evaluating the time (10–30 min) and volume of solvent (1–3 mL).

Extraction conditions: the significance of the parameters that could influence the extraction efficiency was evaluated using a full factorial design, including extraction time (30–60 min), sample pH (4–8) and ionic strength (0–30% w/v of NaCl). After that, the extraction time was studied in a univariate plan, considering 10, 20 and 30 min.

2.6. High throughput RDSE/laminar cork-based procedure

Firstly, all the laminar corks used in this study were weighed (m = 0.030 ± 0.003 g) and conditioned with acetronitrile for 10 min. After the conditioning of the material, the extraction was carried out. Therefore, the disk containing the sorbent material was placed inside a vial containing 35 mL of the sample, containing the analytes. Six magnetic stirrers connected to a tension regulator were used to process the extractions at the same time. After the extraction period of 10 min, the disk was removed and placed in a beaker with 1 mL of MeOH:AcOEt (50:50% v/v). Without the need for evaporation and reconstitution, the resulting extract was kept in a vial until further insertion into the analytical equipment. After desorption, the disk can be reused, requiring only one cleaning step for 5 min and 1 mL of the MeOH:AcOEt (50:50% v/v).

A comparative study was carried out between a traditional technique using cork powder, and a modified technique using a laminar cork. The conditions were set as: 35 mL sample, extraction for 45 min at room temperature and cork sorbent (0.03 g for laminar and 0.005 g for powdered cork - maximum allowable capacity). For the desorption step, the methodology applying powdered cork used 3 mL of solvent, while the methodology with laminar cork needed 1 mL. In both methods it was not necessary to add a solvent drying step.

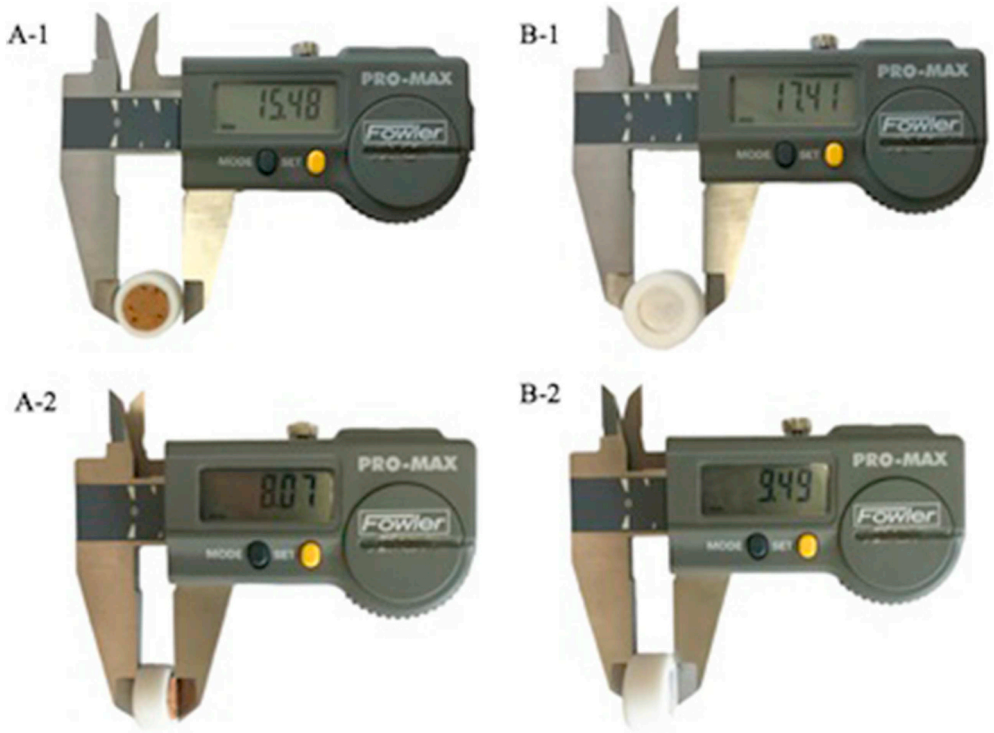

Fig. 1. Comparison between modified and traditional RDSE, with A-1 and A-2 being the height and circumference of the modified disk, respectively, B-1 the circumference and B-2 the height of the traditional disc, respectively.

2.7. Analytical figures of merit and application in environmental aqueous sample

Figures of merit such as linear coefficient of determination, linear range, limit of detection, limit of quantification, accuracy and precision were determined using the optimized extraction conditions. The calibration curves, considering five concentration levels (n = 3), were obtained by plotting the peak area *versus* the concentration of analytes added directly to the sample in a range of 6.25–100 μg L^{-1} for all the analytes, except for EHPABA and MBC, which were added in the range of 2.0–32 μg L^{-1}. The correlation coefficients were calculated based on the calibration curves, and the limits of detection (LOD) and quantification (LOQ) were calculated based on signal-to-noise ratio of 3 (S/N = 3) and 10 (S/N = 10), respectively. The precision of the method was calculated based on the relative standard deviation (RSD). The accuracy (relative recoveries, n = 3) and precision (intra-day, n = 3 and inter-day, n = 9) of the method were evaluated by performing extractions in real water sample spiked at three different concentrations (2.0, 4.0 and 8.0 μg L^{-1} for the EHPABA and MBC and 6.25, 12.5 and 25.0 for the other analytes). The river water sample was collected from the Cubatão River (−27.68939605/-48.73518439) in the metropolitan region of Florianópolis, Santa Catarina, Brazil, using a piezometric collector, and subsequently analyzed.

3. Results and discussion

3.1. Characterization of the cork sorbent

The elemental analysis shows a cork composition of 61.76% of carbon, 8.30% of hydrogen, 0.75% of nitrogen and 29.19% of oxygen. These values are compatible with those reported in the literature [21]. The N_2 adsorption isotherm was determined in order to evaluate the specific surface area and porosity of the laminar cork. The analysis was performed in an entire disk. According to Brunauer classification, isotherms obtained from laminar cork are Type III, where no monolayer formation is identifiable because of the poor adsorbent-adsorbate interactions, characteristic behavior of nonporous or macroporous solids [22]. The specific surface area obtained for laminar cork applying the Brunauer–Emmett–Teller (BET) theory was 2.1 m^2g^{-1}. A similar value was reported in the literature for cork powder with 0.2–0.3 mm of particle diameter and absence of pores using N_2 as adsorbate [21]. Another study achieved specific surface area of 8.2 m^2g^{-1} when a particle size between 400 μm and 1 mm of the cork powder was adopted [23].

Fig. 2 shows the SEM results obtained for the surface evaluation at magnifications of 100 × , 500 × and 1000 × . As can be seen in Fig. 2, the laminar cork used in this work was cut in its cross section and presents a brick wall structure, with parallel alignment rows between the cells [24,25]. As evidenced in Fig. 2C, the cork cells have only external macropores, which confirm the low surface area and isotherm results.

The chemical composition of an adsorbent material influence on the chemical interactions with the target analytes. Cork exhibits a significant hydrophobicity and a number of aromatic rings in its chemical composition (main components are lignin and suberin) which can undergo to π-π interactions with a variety of compounds. Moreover, the external macropores cork cells with brick wall structure, allows for effective physical interaction with the analytes. The modified RDSE methodology uses relatively low volumes of desorption solvent, and all these features can substantially enhance the preconcentration ability of the procedure proposed.

In addition, Fig. S-1 and Table S-2 obtained by thermogravimetric analysis indicate that cork degradation occurred in three stages. The first peak at 53.38 °C corresponds to evaporation and dryness of the material. The second event occurred from 255.81 °C to 351.54 °C and corresponds to 19.72% of weight loss. However, at temperatures between 381.67 and 468.85 °C decomposition equivalent to 55.70% was observed. This great weight loss evidenced in the third event represents the thermal degradation of polysaccharides, such as hemicellulose and cellulose, and the partial degradation of suberin and lignin, which are responsible for the heat resistance of the cork. The resultant residue corresponds to 22.56% of the cork initial mass [21,26]. The ATR-FTIR spectrum of the laminar cork and absorption frequencies of the functional groups of the cork constituents are presented in the supplementary material (Fig. S-2 and Table S-3).

3.2. Extraction efficiency comparison

Firstly, the extraction efficiency of the biosorbent material was evaluated in two ways: laminar and powdered cork. Extractions were performed in order to evaluate which cork format achieved the best chromatographic peak areas of the analytes. Fig. 3 shows the chromatograms of the two cork formats and also a bar graph comparing the extraction efficiency of laminar and powdered cork, respectively.

According to Fig. 3, it is possible to observe that the use of laminar cork as extraction phase presented promising results for the continuation of the work. Under the same extraction conditions, laminar cork presented a significant increase in the extraction efficiency. This can be explained due the amount of extractive phase of at least 10x higher than the cork powdered that fits inside the disk cavity. In this case, the mass gain of the extracting phase achieved using the laminar shape stands out over the larger surface area that owns the cork powder, allowing a significant increase in the analytical signal, without requiring specific apparatus for the evaporation step.

Moreover, in order to evaluate the inter-device reproducibility a univariate approach was performed with six RDSE devices and six different magnetic stirrers connected to a voltage regulator. The inter-device extraction efficiency demonstrates good precision, with RSDs of less than 15% for all the target compounds. This study demonstrated the feasibility of using the RDSE devices containing laminar cork simultaneously allowing for high-throughput analysis.

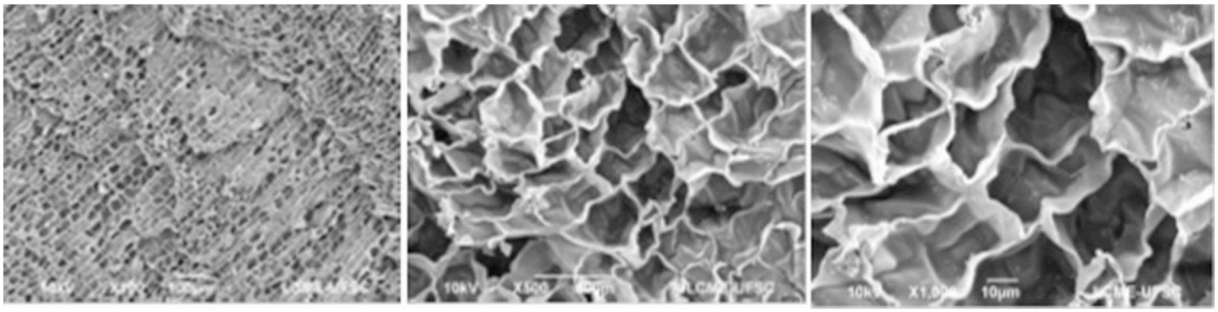

Fig. 2. SEM images of the sorbent cork material at 1000, 50 and 10 μm for the laminar material.

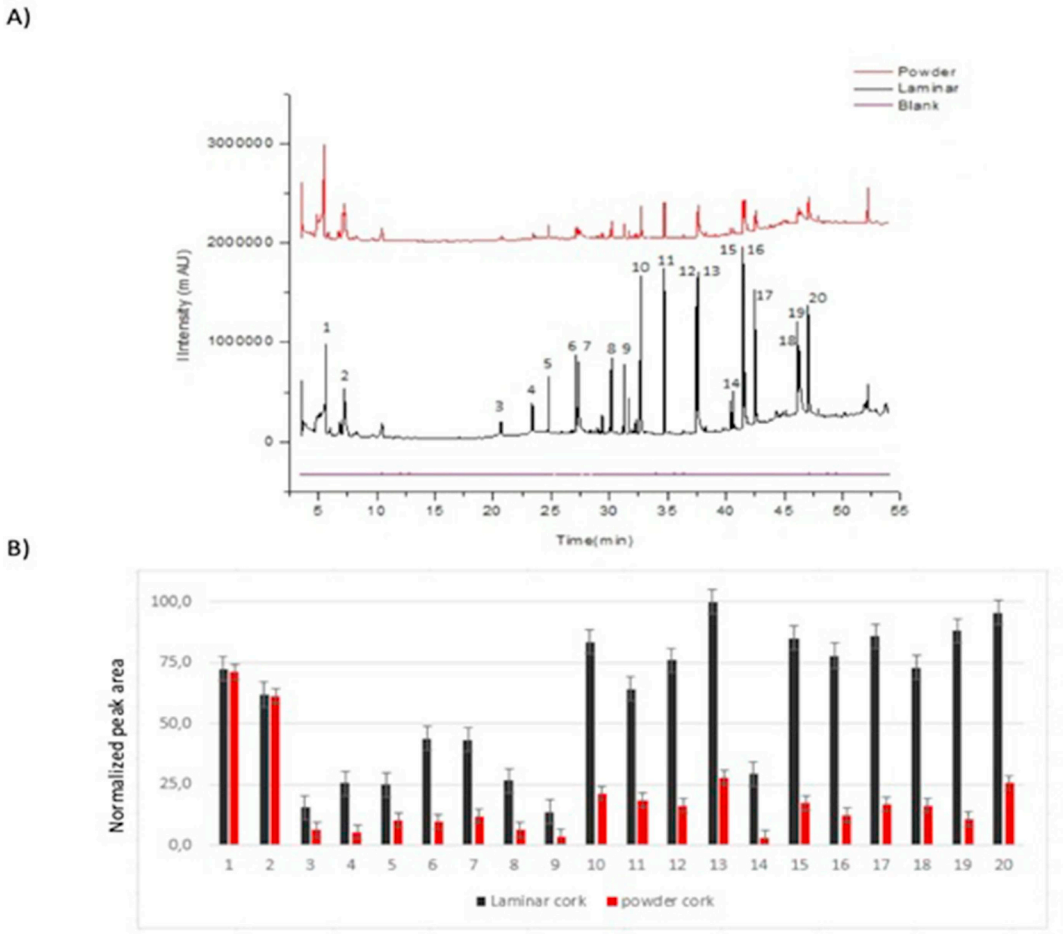

Fig. 3. A) Chromatograms using the laminar cork (black) compared to the cork powder (red). B) Bar graph obtained for the extraction of the analytes at laminar and powdered cork formats. Conditions: 35 mL of ultrapure spiked water with 100 μg L^{-1} of the analytes, pH = 6.0, 45 min of the extraction time and liquid-desorption in 1 mL of methanol for 20 min (Analytes: 1- Ethylbenzene, 2- O-Xylene, 3- Acenaphthylene, 4- Fluorene, 5- Trifluralin, 6- Phenanthrene, 7- Anthracene, 8- Pendimethalin, 9- EHPABA, 10- Pyrene, 11- MBC, 12- Benzo[a]anthracene, 13- Chrysene, 14- Permethrin, 15- Benz(e)acephenanthrylene, 16- Benzo(k)fluoranthene, 17- Benzo(a)pyrene, 18-Dibenzo(a,h)anthracene, 19-Indeno [1,2,3-cd]pyren, 20- Benzo[ghi]perylene). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.3. Optimization of RDSE conditions

3.3.1. Optimization of the liquid desorption step

Desorption is a very important step which needs to be conducted to obtain good desorption efficiency and avoid possible carryover effect. Therefore, the type of desorption solvent, volume and time of desorption required must be carefully optimized.

Firstly, the best solvent or mixture of solvents was evaluated using a simplex-lattice design. The choice of the three solvents evaluated was associated with the polarity of the compounds studied and also regarding the compatibility with the chromatographic system. Fig. 4 shows the surface response of the geometric means of the analytes as a compromise condition obtained by the optimization of the desorption solvent.

The three selected solvents show a range of polarities according to the characteristic of the analytes. (log P: methanol −0.72, acetone −0.45 and ethyl acetate 0.71). The mixture of 50:50 (v/v) of methanol and ethyl acetate exhibited a similar polarity to pure acetone, thus justifying the two regions with excellent extraction efficiencies indicated at Fig. 4. As the extractions were even better using the mixture of methanol and ethyl acetate and because acetone is the most volatile solvent of the three - making sample preparation less easy - the desorption solvent determined was 50:50 (v/v) methanol and ethyl acetate for the continuation of the studies.

After the optimization of the desorption solvent, time of desorption and volume of solvent were evaluated using a Doehlert design. The smallest amount of desorption solvent should be used to avoid excessive dilution of the analytes. Thus, 1 mL of a mixture of 50:50 (v/v) AcOEt:MeOH was selected, since it provided the lowest dilution of the analytes. As the analytes have a good affinity for the desorption solvent, low desorption times were sufficient to remove them from the extractive phase (Fig. 5). Thus, 20 min was used for the desorption time, guaranteeing an efficient desorption. So, the best results were obtained with 20 min of desorption and 1 mL of solvent.

In addition, to evaluate the carryover effect, a second desorption was performed and injected into the chromatographic equipment. The chromatograms did not present corresponding analyte peaks, indicating that the desorption process was efficient and an additional step of cleaning the material is not required.

3.3.2. Optimization of the extraction conditions

In order to evaluate the variables that can influence the extraction efficiency, a full factorial design involving sample pH, extraction time and salt addition was performed, totalizing 8 experiments. The Pareto

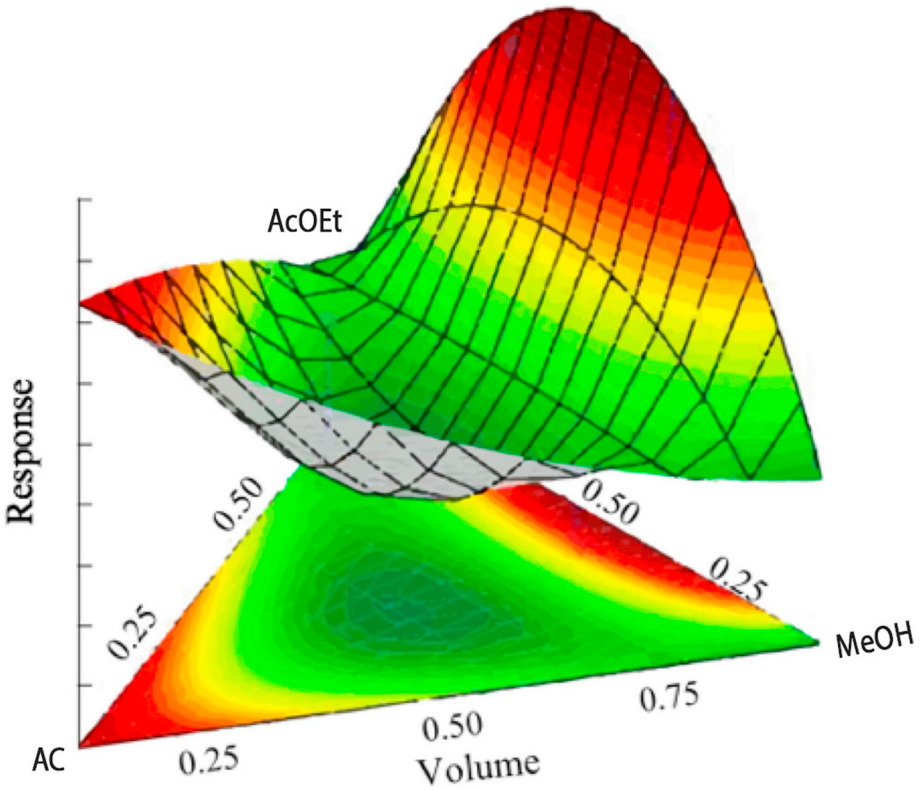

Fig. 4. Centroid Simplex surface for desorption solvent optimization. Conditions: 35 mL of ultrapure spiked water with 100 μg L^{-1} of the analytes, pH = 6.0, 45 min of the extraction time and liquid-desorption in 1 mL for 20 min.

chart obtained and Anova Table can be seen in the Supplementary Information (Fig. S-3 and Table S-4).

The pH of the samples affects the dissociation of the analytes as well as the extraction efficiency. As the target compounds do not ionize in the usual pH range (except for EHPABA, whose pka is close to 2.9 [22]), this parameter could be evaluated according to the expected pH for wastewater (values ranging from 4 to 8) because in this range, all the 20 analytes are in their neutral form. As can be seen in Fig. S-3, the Pareto chart showed that for this pH range there is no significant difference in the extraction efficiency, therefore no adjustment of pH was necessary

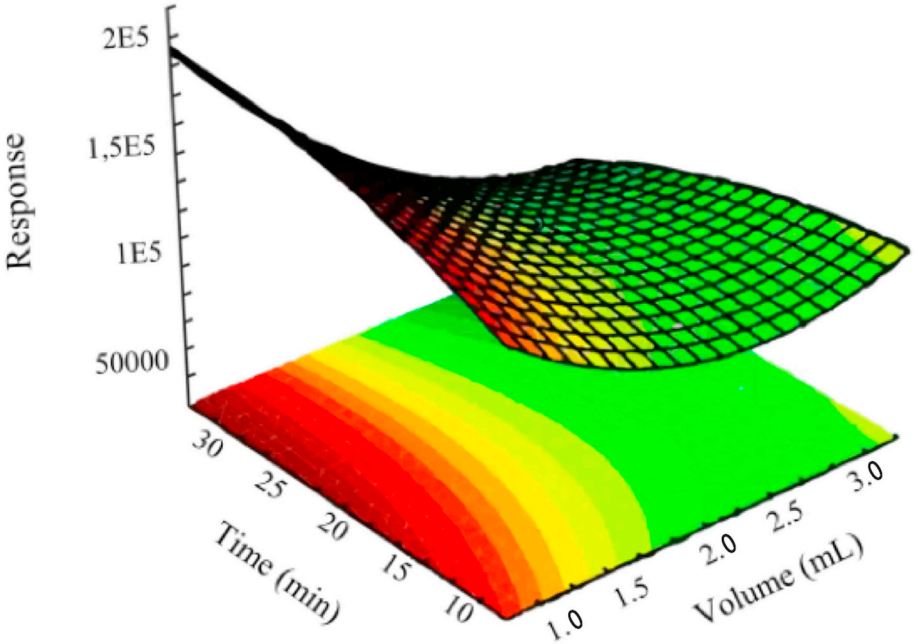

Fig. 5. Doehlert surface for determination of optimum solvent volume and desorption time (R:0.9787). Conditions: 35 mL of ultrapure spiked water with 100 μg L^{-1} of the analytes, pH = 6.0, 45 min of the extraction time and liquid-desorption in 1 mL of MeOH: AcOEt (50:50 v/v) for 20 min.

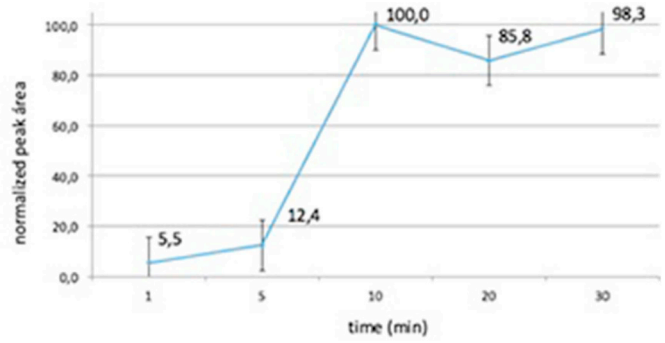

Fig. 6. Univariate study for the extraction time to evaluate the parameter in times lower than 30 min.

for the development of this methodology, since, in common surface water, all analytes are non-ionized.

The use of salt increases the ionic strength of the sample, leading to the salting-out effect, which makes it easier for the semi-polar and polar analytes to migrate from the sample to the sorbent. In contrast, it may hinder the diffusion of the analytes by the sample. Salt addition studies were not significant, so the optimized condition for this variable was chosen without salt addition.

According to the Pareto chart it is possible to observe that the time selected as the domain for the study of the parameter exceeded the ideal values for the extraction. This occurs because after reaching equilibrium, extra times will not significantly improve the signal of the analytes. In this way, an improved optimization of time had to be performed.

A univariate optimization of this variable was performed to evaluate significant differences in extraction times of less than 30 min. The result of this optimization is shown in Fig. 6, with 10 min selected as the optimum extraction time. After this time, a plateau affect is observed, not requiring longer extraction times.

The optimized RDSE procedure consisted of 35 mL of sample and extraction time under constant agitation for 10 min. After that, the liquid desorption was performed in a beaker containing 1 mL of MEOH: AcOEt (50:50 v/v) for 20 min.

3.4. Validation parameters

The analytical figures of merit obtained in this study are shown in Table 1. The linear coefficient of determination (R^2) was higher than 0.9915, which indicates good linear fit. Values for LOD and LOQ were obtained without the evaporation step, confirming the proposed methodology for the quantification of analytes in accordance with current Brazilian Legislation. Moreover, satisfactory results for the method precision were achieved. Intra-day and inter-day precision presented RSD values less than 19.5% and 20.0%, respectively (Table 1).

The accuracy of the method, using three different analyte concentrations, was determined based on the relative recoveries. As also shown in Table 2, the relative recoveries ranged from 80.1 to 119.8%. When the non-spiked sample was analyzed none of the target analytes was observed in the chromatogram.

Finally, the proposed method was compared with other methods previously reported in the literature for the determination of the target compounds. As shown in Table 3 it is possible to observe that the proposed method presents excellent results using cork, a renewable and low-cost biosorbent. Methods with low quantification limits require a drying step or high sample preparation time. The developed method has acceptable limits of quantification considering the rapidity of the sample preparation. By adding an evaporation step, better limits could still be explored. In this study, the analysis throughput for this methodology was substantially increased due to the coupling of six magnetic stirrers, which enabled a total extraction time of only 5 min per sample turnaround times.

4. Conclusions

The methodology developed using a high throughput RDSE/laminar cork-based procedure modification was successfully optimized, exhibited very satisfactory analytical performance and presented better results than the classic technique using sorbent powder. The new configuration of the apparatus is simple to use, reusable and requires small amounts of organic solvent, contributing to the development of a green methodology. In addition, the optimization of the method allowed the extraction of different micro-pollutants, making it possible to explore the modified technique for the application in different samples. The proposed methodology presents results according to the current Brazilian Legislation, even without the evaporation step. However, to improve the LOQ and LOD, an evaporation step could be added, while still maintaining high throughput.

Table 1
Analytical figures of merit of the proposed method.

Analyte	Linear Range (μg L^{-1})	Linear Equation	R^2	LOD[a] (μg L^{-1})	LOQ[b] (μg L^{-1})
Ethylbenzene	6.25–100	y = 380.23x - 1379.8	0.9975	0.60	2.02
O-Xylene	6.25–100	y = 299.37x - 484.96	0.9923	0.37	1.22
Acenaphthylene	6.25–100	y = 1011.9x - 2366.9	0.9973	0.24	0.81
Fluorene	6.25–100	y = 849.82x - 33.042	0.9929	0.38	1.28
Trifluralin	6.25–100	y = 141.29x + 30.833	0.9992	1.44	4.81
Phenanthrene	6.25–100	y = 670.7x – 2192.3	0.9939	0.29	0.96
Anthracene	6.25–100	y = 1972x – 8547.8	0.9961	0.15	0.52
Pendimethalin	6.25–100	y = 89.245x – 33.042	0.9993	1.50	5.00
EHPABA	2.00–32.0	y = 91.533x + 204.29	0.9929	0.51	1.72
Pyrene	6.25–100	y = 2957.4x – 2150.3	0.9984	0.09	0.29
MBC	2.00–32.0	y = 1592.6x – 998.54	0.9992	0.14	0.46
Benzo[a]anthracene	6.25–100	y = 604.31x + 6301.1	0.9996	0.09	0.31
Chrysene	6.25–100	y = 3392.4x – 17821	0.9951	0.12	0.39
Permethrin	6.25–100	y = 156.16x – 747.17	0.9915	1.26	4.19
Benz(e)acephenanthrylene	6.25–100	y = 714.01x + 3869.8	0.9954	0.16	0.55
Benzo(k)fluoranthene	6.25–100	y = 1870.4x – 2198	0.9919	0.11	0.37
Benzo(a)pyrene	6.25–100	y = 2808.4x – 7574.5	0.9917	0.13	0.44
Dibenzo(a,h)anthracene	6.25–100	y = 1472.8x – 7797.7	0.9953	0.18	0.62
Indeno [1,2,3-cd]pyren	6.25–100	y = 200.27x – 567.19	0.9940	0.80	2.68
Benzo[ghi]perylene	6.25–100	y = 1464.4x – 4854.8	0.9937	0.15	0.49

[a] LOQ and [b] LOD values were calculated based on signal-to-noise ratios of 10 (S/N = 10) and 3 (S/N = 3), respectively.

Table 2
Relative recoveries of analytes and precision (inter and intra-day[a]).

Analyte	Ethylbenzene			O-Xylene			Acenaphthylene			Fluorene		
Added	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**
Rec (%)	109.1	103.7	93.9	113.7	108.1	80.1	100.2	102.0	114.9	83.6	85.6	99.2
Intra-day (%) (n = 3)	1.23	1.82	0.52	10.75	3.46	10.70	3.09	2.04	4.90	0.57	3.11	7.33
Inter-day (%) (n = 9)	17.22	19.58	13.78	7.64	3.96	7.73	8.60	15.64	19.88	5.27	11.19	5.18
Analyte	**Trifluralin**			**Phenanthrene**			**Anthracene**			**Pendimethalin**		
Added	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**
Rec (%)	103.9	106.3	98.8	104.0	96.2	81.9	104.0	96.2	81.9	90.5	119.8	113.0
Intra-day (%) (n = 3)	0.30	1.25	2.14	5.05	19.40	3.91	5.05	19.40	3.91	9.59	3.84	1.66
Inter-day (%) (n = 9)	19.91	1.06	13.75	18.93	17.56	19.04	18.93	17.56	19.04	7.43	5.06	4.62
Analyte	**EHPABA**			**Pyrene**			**MBC**			**Benzo [a] anthracene**		
Added	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**
Rec (%)	90.5	119.8	113.0	89.4	96.5	95.5	80.4	100.0	107.3	109.1	101.6	92.7
Intra-day (%) (n = 3)	9.59	3.84	1.66	2.06	19.22	2.37	4.57	18.23	18.17	7.92	15.24	2.34
Inter-day (%) (n = 9)	7.43	5.06	4.62	14.11	18.53	17.22	5.24	12.64	12.84	5.64	15.24	8.94
Analyte	**Chrysene**			**Permethrin**			**Benz(e)acephenanthrylene**			**Benzo(k)fluoranthene**		
Added	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**
Rec (%)	109.9	95.8	89.8	119.8	114.2	84.5	84.6	115.6	111.6	91.3	112.1	83.5
Intra-day (%) (n = 3)	3.90	14.17	9.92	15.04	3.81	4.60	9.68	15.14	2.72	12.73	2.80	6.56
Inter-day (%) (n = 9)	10.90	10.13	7.54	18.59	2.64	15.02	19.32	5.77	2.07	8.99	13.06	4.62
Analyte	**Benzo(a)pyrene**			**Dibenzo(a,h)anthracene**			**Indeno [1,2,3-cd]pyren**			**Benzo [ghi] perylene**		
Added	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**	**6.25**	**12.5**	**25**
Rec (%)	87.5	104.8	114.6	114.3	111.1	82.4	110.7	112.6	86.4	116.6	107.5	84.1
Intra-day (%) (n = 3)	19.65	9.50	16.77	16.13	11.67	0.27	16.56	3.36	13.92	13.25	16.92	2.25
Inter-day (%) (n = 9)	16.17	7.64	11.78	18.30	10.92	2.02	10.85	2.51	10.72	15.16	16.33	8.23

[a] Intra-day and inter-day precisions were calculated based on the relative standard deviation (RSD).

Table 3
Comparison of the analytical features for the RDSE and other sorbent extraction approaches with data reported in the literature for the analytes with similar characteristics and the same matrix. Extraction techniques: SBSE: Stir bar sorptive extraction; SBSDuE: stir bar sorptive–dispersive microextraction.

Technique	Instrumentation	Analytes	Extraction phase	LOQ ($\geq \mu g\ L^{-1}$)	Evaporation step	Total extraction time per sample (min)	Reference
RDSE	GC-MS	parabens	OASIS HLB	0.15	Yes	80	[16]
RDSE	UPLC-MS/MS	pesticides	OASIS HLB	0.05	Yes	140	[17]
RDSE	GC-ECD	PCBs	MMT – IL	0.0065	Yes	40	[20]
RDSE	LC-UV	acid drugs	C18 modified	72.4	Yes	26	[27]
RDSE	GC-MS	drugs	OASIS HLB	0.007	Yes	110	[19]
RDSE	GC-MS	diclofenac and mefenamic acid	MIP phase	0.20	Yes	130	[28]
DSE	UHPLC-UESI-TOF-MS	drugs	OASIS HLB	0.009	Yes	70	[29]
RDSE	GC-MS	pesticides	PDMS	1.61	Yes	210	[18]
SBSDμE	GC-MS	MBC	MNPs	0.078	No	35	[8]
SBSE	HPLC-FLD	PAH	Sand	0.79	No	65	[30]
RDSE	GC-MS	pesticides	Laminar cork	< 5.0	No	5	This study
		MBC		0.47			
		Indeno [1,2,3-cd]pyrene		2.58			
		PAH (others)		< 1.28			

OASIS HLB: Hydrophilic-Lipophilic-Balanced reversed-phase sorbent; MMT – IL: Montmorillonite modified by ionic liquids; PDMS: Polydimethylsiloxane; MIP: Molecularly imprinted polymer; MNPs: Magnetic nanoparticles.

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Appendix A. Supplementary data

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