

A Green Procedure Using Disposable Pipette Extraction to Determine Polycyclic Aromatic Sulfur Heterocycles in Water Samples and Solid Petrochemical Residues

Karine O. Garcia,^a Morgana Frena,^a Otávio R. Bittencourt,^a Hérica A. Magosso,^a
Eduardo Carasek^a and Luiz A. S. Madureira^{✉*}^a

^aDepartamento de Química, Universidade Federal de Santa Catarina, Campus Universitário
Trindade, 88040-900 Florianópolis-SC, Brazil

A simple and efficient method using reduced amounts of solvents for the determination of polycyclic aromatic sulfur heterocycles (PASHs) in aqueous matrices from a lagoon and leachate solid waste from a petrochemical industry is proposed. The target analytes were previously concentrated using the disposable pipette extraction (DPX) technique applying gas chromatography-mass spectrometry (GC-MS) for analysis. In this innovative approach, the DPX was modified with 8-hydroxyquinoline silica gel immobilized with Pd^{II} for the pre-concentration of 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene, 1,2-naphthobenzothiophene, 2-methylbenzothiophene and 3-methylbenzothiophene. To improve the extraction efficiency, parameters such as desorption solvent, ionic strength, extraction and desorption cycles were optimized. The values obtained for the limits of detection (LOD) and quantification (LOQ) are adequate for the determination of PASHs in aqueous and leachate solid waste samples. Precision and accuracy parameters showed satisfactory results, providing relative recoveries of 74.6-131.2% for PASHs from lagoon water samples and 72.7-118.0% for leachate of solid waste samples. In the lagoon samples the relative standard deviation (RSD) values for the five PASHs ranged from 0.3 to 9.2% and 3.8 to 19.4% for the leachate of the solid waste. These results demonstrate that the proposed method represents a promising alternative for the determination of PASHs in aqueous and leachate solid waste samples.

Keywords: DPX, PASH, 8-HQ-Pd silica gel, water, solid waste

Introduction

Crude oils are extremely complex mixtures of organic compounds predominantly composed of aliphatic and aromatic hydrocarbons, resins and asphaltene. Asphaltene and resins are heavy N,S,O-containing molecules (molecular weight > 500), whereas hydrocarbons are usually of lower molar mass. The term hydrocarbon can be applied to compounds containing not only H and C but also S, O and N atoms, since other molecules can be found in the hydrocarbon fractions isolated by chromatographic procedures.¹ Sulfur is often the most abundant heterogeneous element in crude oils, with contents ranging from 0.05-14% by mass.²⁻⁴

Sulfur-containing polycyclic aromatic heterocyclic compounds (PASHs) are an important chemical class of organosulfur compounds in petroleum, being employed as a potential indicator of the maturity of crude oils and

their source rocks. There has recently been a growing interest in PASHs in relation to a number of issues, including pipeline corrosion and catalyst poisoning.^{3,5} Since many of these compounds have been reported to show toxic, mutagenic and carcinogenic activity, attention must be given even when present at low concentrations in petrochemical residues and the aqueous phase in special after oil spills.⁶⁻⁹

Sulfur compounds present in crude oils are difficult to identify and quantify. The PASH substituent structures and molecular ring size are similar to those of polycyclic aromatic hydrocarbons (PAHs), normally present in crude oil and oil spills at much higher concentrations, making difficult the isolation and quantification of PASHs.^{3,10} Several methods for the separation and characterization of PASHs in crude oil have been reported,^{3,6,7,10-12} but a few studies have been conducted with aqueous matrix.¹³⁻¹⁵

PASHs are molecules of a hydrophobic nature with a tendency to accumulate in sediments and animal tissues. However, because of the toxic effects to both environment

*e-mail: luiz.madureira@ufsc.br

and human health, here we propose to apply the Brazilian Standard normative (ABNT NBR 10004/2004)¹⁶ to assess the presence of PASHs in petrochemical residues using the proposed method. For solid waste, the Brazilian normative set a maximum limit of organic compounds in extracts obtained in leaching tests. Despite not being part of the ABNT NBR 10004/2004¹⁶ list of toxic organic contaminants, it is important to evaluate potential sources of PASHs contamination since a great quantity of petrochemical residues is worldwide generated every year and has to be properly disposed.

Conventional chromatographic methods require improvements in the clean-up procedure, including reductions in sample preparation time and the amount of toxic solvent used. Thus, more attention is being given to the development of simple clean-up steps. In recent years, as an alternative to solid phase extraction (SPE), disposable tip extraction, known simply as DPX (disposable pipette extraction), was developed and proven to be an attractive option, being a fast, simple, low-cost and environmentally-friendly technique.

The DPX is a solid phase extraction technique derived from SPE.¹⁷ It consists of a pipette (1 or 5 mL) containing an extraction phase (sorbent) dispersed between two filters. The standard procedure is relatively simple and include the following steps: (i) conditioning to activate the sorbent sites; (ii) sample aspiration; (iii) air aspiration to allow a dynamic mixture between the sorbent and the sample; (iv) sample disposal; (v) aspiration and disposal of solvent to remove possible interfering compounds; and (vi) solvent aspiration followed by air aspiration for the liquid desorption of the analytes. A rapid equilibrium is established between the sorbent phase and the sample due to the aspiration of air. Parameters such as number of cycles of extraction/desorption, time of each cycle, solvent for conditioning and elution steps are commonly optimized according to type of sorbent and analytes.¹⁷⁻²² Hence, advantages using DPX include rapid extraction along with the use of a small mass of the sorbent phase and low volumes of organic solvent and sample, thus adhering to green chemistry principles.^{23,24}

Several environmental applications have been reported including the determination of pesticides in fruits and vegetables,²⁵ palladium in liquid residues,²⁶ polychlorinated biphenyls in small-size biological tissue samples,²⁷ PASHs in marine crude oils,³ explosives in water,²⁸ phenolic endocrine-disrupting compounds,²⁰ pesticides in human urine²⁹ and emerging contaminants in lake water samples.²¹ However, studies involving the extraction of PASHs in water using DPX have not been reported in the literature. In this study, an extraction procedure using DPX is proposed

for the determination of five PASHs in water and applied to samples taken from a lagoon and leachate from solid waste samples quantified with gas chromatography-mass spectrometry (GC-MS).

Experimental

Materials and reagents

A total of four surface water samples were collected using clean amber glass bottles. Samples were taken from the Patos Lagoon, Rio Grande do Sul, Brazil, near a marine in a region with intense traffic of boats (Supplementary Information (SI) section, Figure S1). These samples were kept refrigerated and extracted up to three days after collection. Three samples containing petrochemical residues provided by a petroleum hydroprocessing unit were submitted to the leaching procedure as described by the Brazilian Standard (ABNT NBR 10005/2004).³⁰

The acetone (Panreac, Barcelona, Spain), ethyl acetate (Vetec, Rio de Janeiro, RJ, Brazil), *n*-hexane (Tedia, Fairfield, CA, USA), methanol (Tedia, Fairfield, CA, USA) and toluene (J.T.Baker, Mallinckrodt, NJ, USA) were of chromatographic grade. Acetic acid (Vetec, Rio de Janeiro, RJ, Brazil), analytical grade, and high purity distilled and deionized water (Milli-Q Millipore Bedford, MA, USA) were used to prepare the extraction solution (pH 2.88) as recommended by the ABNT NBR 10005/2004.³⁰ Buffer solutions at pH 4.00 ± 0.02 (Nuclear, Diadema, SP, Brazil) and pH 7.00 ± 0.02 (Synth, Diadema, SP, Brazil) were used for the pH meter calibration. Silica gel with a particle diameter of 70-230 mesh (Merck, Darmstadt, Germany), 3-aminopropyl triethoxysilane (Sigma-Aldrich, Hong Kong, China), 8-hydroxyquinoline (Merck, Darmstadt, Germany), paraformaldehyde (Sigma-Aldrich, Steinheim, Germany), palladium(II) chloride (Aldrich, St. Louis, MO, USA), and ethyl alcohol were of analytical-reagent grade. The PASH standards (Aldrich, St. Louis, MO, USA) used were 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene, 1,2-naphthobenzothiophene, 2-methylbenzothiophene and 3-methylbenzothiophene.

Plastic pipette tips (1 mL, without sorbent material) were purchased from DPX Labs (Columbia, SC, USA).

Apparatus

The analytical procedure was conducted on a GC-MS system consisting of GC Clarus 680 and MS Clarus SQ8 instruments (PerkinElmer, Shelton, CT, USA). Separations were carried out using an Elite-5MS capillary column (30 m, 0.25 mm inner diameter, 0.25 µm film thickness)

(PerkinElmer, Shelton, CT, USA) under the following conditions: injector temperature 250 °C (splitless mode; 1 min); oven temperature program starting at 40 °C (held for 4 min), increasing at 6 °C min⁻¹ up to 300 °C (held for 5 min). The GC-MS interface and the ionization source temperature were set at 250 and 200 °C, respectively. Helium (99.999% purity) was used as the carrier gas at a flow rate of 1.0 mL min⁻¹. MS ionization was operated under electron ionization (EI) mode at 70 eV. Analysis was performed in selected ion monitoring (SIM) mode, using the ions (*m/z*): 74, 147, 148, 149, 189, 197, 198, 199, 211, 212, 213, 234 and 235. Figure 1 shows the chromatogram of the method for the fortified leachate.

Synthesis of sorbent material

The sorbent material has been synthesized according to Yang *et al.*³ Briefly, approximately 0.3 g of 8-hydroxyquinoline (8-HQ) was weighed and dissolved in 10 mL ethanol, while being slightly heated (in a glycerine bath at 60 °C). The volume was then made up to 20 mL and

0.1 g of paraformaldehyde was added followed by 0.5 mL of 3-aminopropyl triethoxysilane. The last step consisted of the addition of 1.0 g of pure silica. The mixture was heated and moderately stirred in periods of 1 h as each reagent was added, totaling approximately 6 h of reaction. The modified silica was dried at 100 °C for 2 h, washed with ethanol using Soxhlet for 24 h and then dried at room temperature. The 8-HQ silica gel was further treated with 150 mL of an aqueous solution of palladium chloride (0.01 mol L⁻¹) under stirring for 8 h to obtain 8-HQ-Pd silica gel. The solid material was then decanted and washed with deionized water.

Characterization of the sorbent phase

For the characterization of the sorbent material (8-HQ silica gel immobilized with Pd^{II}), thermogravimetric analysis (TGA) was performed under nitrogen flow in a Shimadzu TGA-50 thermogravimetric analyzer, operating from ambient temperature to 700 °C with a heating rate of 10 °C min⁻¹.

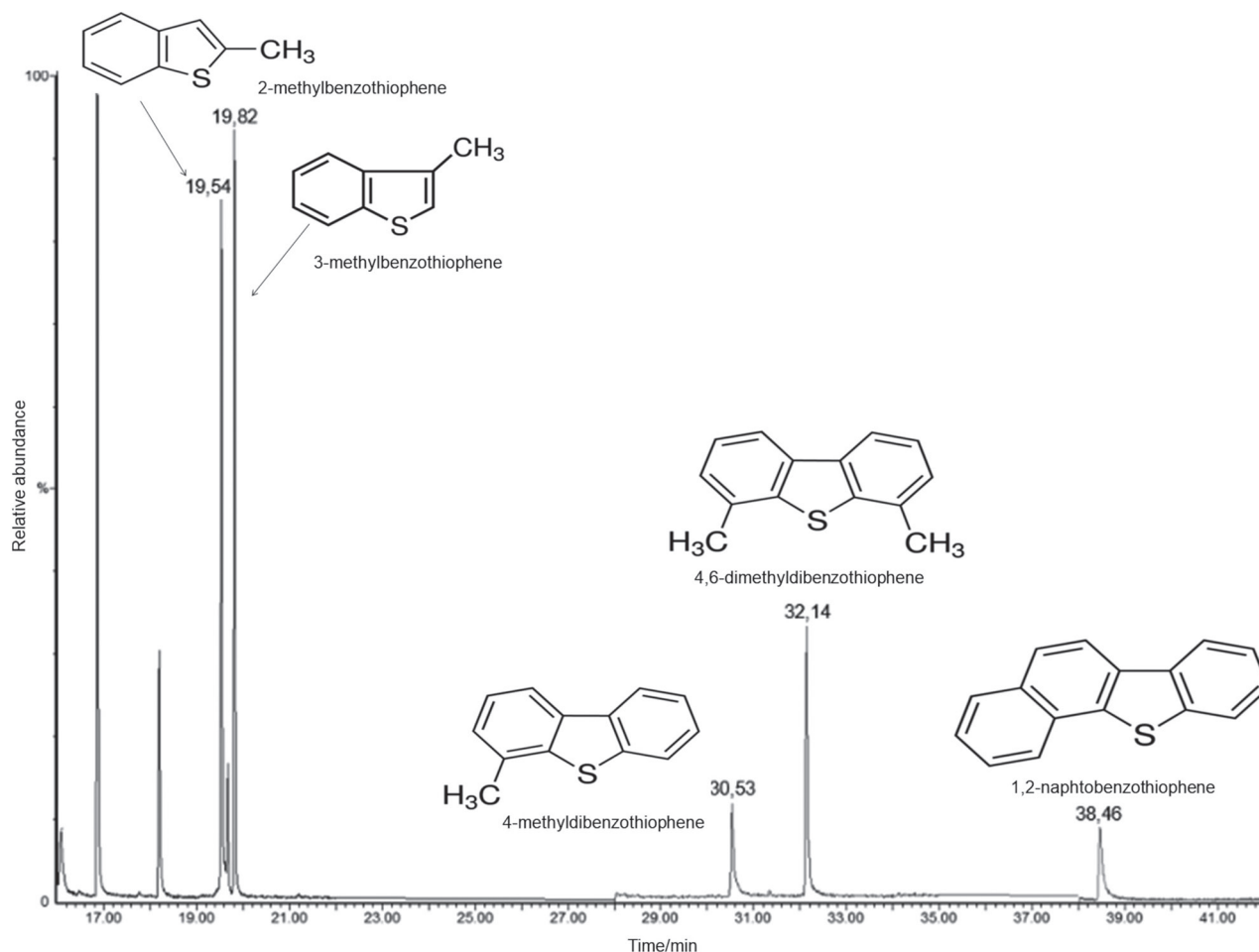


Figure 1. Chromatogram of the leachate fortified with the PASH mix at a concentration of 100 µg L⁻¹ after extraction with DPX under optimized conditions, with selected ions *m/z*: 74, 147, 148, 149, 189, 197, 198, 199, 211, 212, 213, 234 and 235.

The morphology of the 8-HQ-Pd silica gel was evaluated by scanning electron microscopy (SEM). The sorbent was dispersed on double-sided tape on an aluminum support and covered with a thin film of gold. The micrographs were obtained using a Hitachi TM 3030 microscope (Tokyo, Japan), coupled to an energy dispersive X-ray spectroscopy (EDS) detector.

Nuclear magnetic resonance (NMR) spectra of ^{29}Si and ^{13}C were obtained using a Varian VNMRs spectrometer operating at a frequency of 400 MHz and chemical shifts (δ) were expressed in parts *per* million (ppm). For the XRD analysis, the experiments were performed using powdered samples at room temperature, with a Bruker DDR Phaser XRD with a copper source.

Optimization of DPX procedure

Extractions were performed using 700 μL of ultrapure water spiked with a standard mixture at a concentration of 5 $\mu\text{g L}^{-1}$. The sample volume was kept constant at 700 μL to allow a satisfactory dynamic mixture between the sorbent phase (the mass of sorbent phase was fixed at 20 mg) and the aqueous sample inside the pipette (1 mL capacity). For the desorption step, the volume of organic solvent was kept constant (200 μL). The time of each extraction/desorption cycle was fixed at 30 s. Experiments were performed in a single aliquot and each cycle represents one solvent aspiration. These parameters were established based on previously reported studies in which DPX was used as the sample preparation technique.^{3,18,20,27,28}

Optimizations of desorption solvent and number of extraction/desorption cycles

The desorption solvent efficiency was optimized using a univariate method and acetone, ethyl acetate, *n*-hexane, methanol and toluene were investigated. In this procedure, 200 μL of each solvent and 5 desorption cycles for the same aliquot have been employed.

Prior to the extractions, the sorbent phase was conditioned applying 5 cycles with methanol and 3 cycles with ultrapure water. The optimization of the number of extraction cycles (from 1 to 11) and desorption cycles (from 1 to 11) was carried out with a multivariate strategy, using a central composite design. Five levels of each variable were studied, including a triplicate center point. Blank samples were also evaluated. Statistical procedures were performed using the Statistica 6.0[®] computer program.³¹ The number of extraction cycles was optimized using 700 μL of ultrapure water spiked with 4-methyldibenzothiophene (5 $\mu\text{g L}^{-1}$). The number of desorption cycles was optimized using

200 μL of methanol. The influence of the ionic strength on the extraction efficiency was evaluated varying the NaCl concentration from 0 to 25% (m v^{-1}).

Leaching of the solid waste

The leaching process was carried out according to the procedure recommended in the Brazilian Standard (ABNT NBR 10005/2004).³⁰ In summary, to a sample aliquot of 12.5 g, 250.0 mL of the appropriate extraction solution containing 0.57% (v v^{-1}) glacial acetic acid at pH 2.88 ± 0.05 were added. This solution is adequate for the extraction of volatile compounds. The mixture was submitted to stirring by rotating at 30 ± 2 rpm with an appropriate stirrer (TE-743, Tecnal, Piracicaba, SP, Brazil) for 18 h and the leachate was then ready for analysis.

Quality assurance/quality control of the method and application

Quality assurance/quality control of the method was carried out by obtaining the main method parameters, namely, linear range, correlation coefficient and limits of detection and quantification (LOD and LOQ). The LOD was defined as being 3 times the ratio of the standard deviation (s) of the lowest point on the analytical curve to the angular coefficient of the curve (a) while the LOQ was defined as being 10 times this ratio. Precision was evaluated as the relative standard deviation of three replicate analyses and the accuracy through relative recovery tests.

Results and Discussion

Sorbent selection and characterization

Sorption is a crucial step that affects the separation process. Thus, a relatively simple route was selected for this study, using the 8-HQ sorbent immobilized on silica, since this has been found to be a particularly useful material for metal chelating applications.³² The sorbent is anchored on the surface of the previously aminated silica by a one-step Mannich reaction, as described by Zheng *et al.*³²

The extraction time is considerably reduced in this route compared to other techniques. For example, pre-fractionated techniques using ligand exchange chromatography (LEC),^{7,15,33} SPE¹³ and solid phase microextraction (SPME)³⁴ can be disadvantageous due to longer time for pre-concentration and desorptions and also, in the case of LEC and SPE, high consumption of solvents, which are significant drawbacks in the analysis of large sets of samples. Also, sulfur ligands present an exceptional

affinity toward Pd^{II}. Thus, Pd^{II} in the composition of the sorbent enables the selective separation of PASHs from PAHs and also eliminates the decomplexing step, since Pd^{II} is chemically bound to the silica surface.

The characterization of 8-HQ silica immobilized with Pd^{II} was performed by TGA and SEM (Figures 2 and 3). The TGA curve for the sorbent material showed two different temperature regions. The total loss of organic matter was approximately 15%. In the temperature region from 25 to

150 °C there is a well-defined peak with a mass loss of around 2.6%, corresponding to the solvent (ethyl alcohol) used during the synthesis of the sorbent material. The main mass loss occurred at between 250 and 550 °C, where a second peak representing 12.9% of the total mass was observed. This loss corresponds to the ligand of interest that had not reacted during the synthesis. The SEM image shown in Figure 3 confirms the irregular structure expected for the synthesized material.

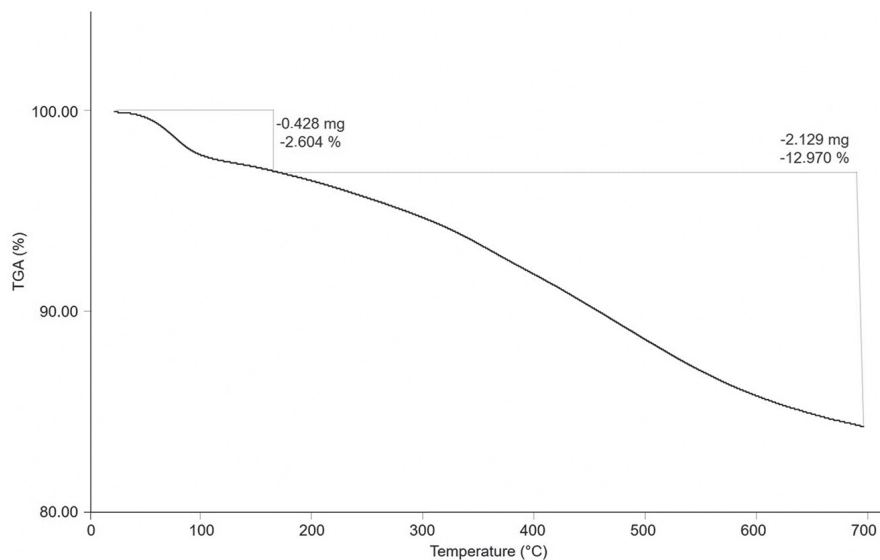


Figure 2. Thermogravimetric profile of the 8-HQ silica immobilized with Pd^{II}.

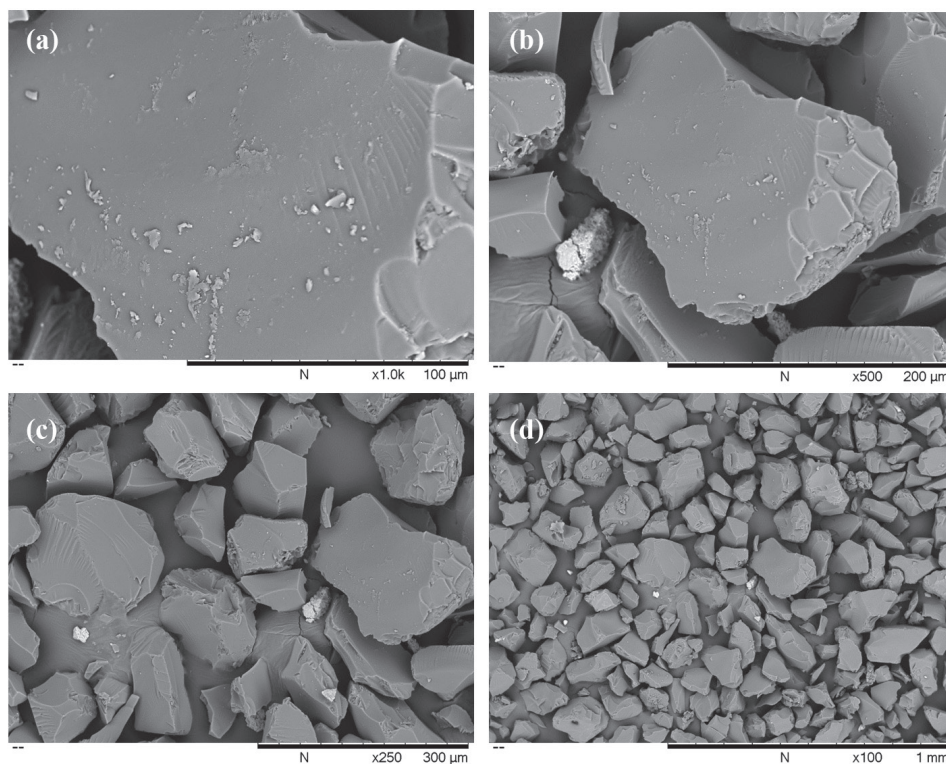


Figure 3. SEM micrographs obtained with the 8-HQ silica immobilized with Pd^{II} at magnifications of (a) 1000×, (b) 500×, (c) 250× and (d) 100×.

From the EDS analysis, the presence of approximately 0.01%, by mass, of Pd adsorbed on the material structure can be observed. It is worth mentioning that the amount of carbon observed in this analysis is slightly higher than expected, this is most likely due to the fact that the tape used in the sample preparation is made of carbon and because of that, it cannot be more accurate in the mass of the adsorbed Pd (Figure S2, SI section).

As a complementary technique, solid NMR analysis was performed to attest the modification of the silica gel after the synthesis. Based on the ^{29}Si spectra, it can be seen that the 8-HQ was chemically bonded to the silica gel, since the bands at -59 and -65 ppm organosilane characteristics are present in the analyses performed after the reaction with the commercial silica (Figure S3a, SI section).³⁵ According to the ^{13}C spectra, bands referring to 8-HQ incorporation can also be observed in the final material analysis (Figure S3b, SI section).

Using X-ray diffraction (XRD) analysis, the amorphous characteristic of the 8-HQ-Pd silica gel was observed. However, no significant difference was detected with the small amount of PdCl_2 added, indicating the high dispersion in the silica amorphous matrix (Figure S4, SI section).

From the results of the characterization analyzes it can be observed the presence of Pd in the sorbent material and its structure. Hence, these analyzes were considered satisfactory for the characterization of the sorbent material.

Solvent desorption optimization

The optimization of the desorption condition was firstly

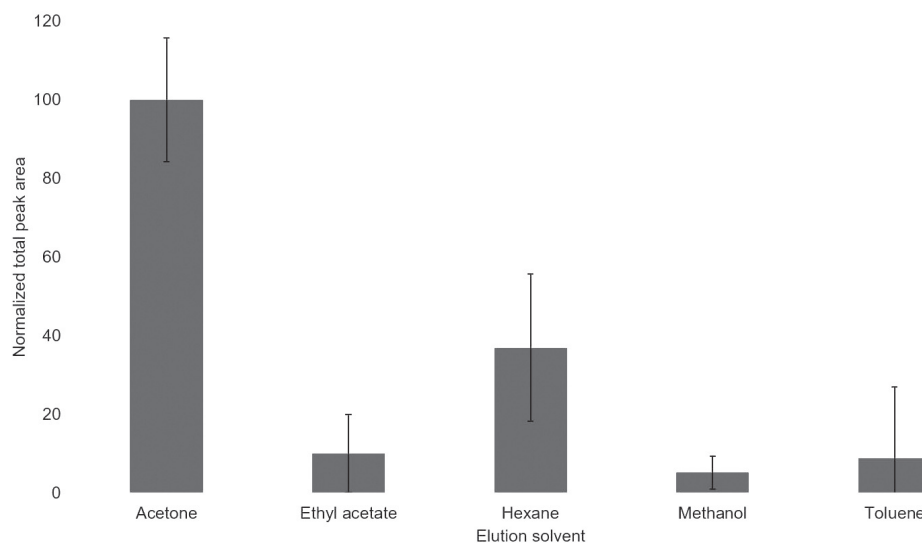


Figure 4. Bar graph for the optimization of the desorption solvent. Experimental conditions: 700 μL of ultrapure water spiked with 500 $\mu\text{g L}^{-1}$ of PASHs mix, 5 cycles of 30 s for the extraction, 20 mg of 8-HQ immobilized with Pd^{II} as sorbent phase, desorption with 200 μL of methanol, 5 desorption cycles of 30 s (each experiment was performed in triplicate).

performed to ensure that the analytes were efficiently desorbed from the sorbent phase to avoid any carryover effect. The following solvents were evaluated: acetone, ethyl acetate, *n*-hexane, methanol and toluene. Figure 4 shows that the best response was achieved with acetone, eluting a higher amount of all analytes compared to the other solvents, possibly due to the higher solubility of the analytes, and acceptable standard deviation bars related to the variation of the five analytes for each solvent.

Optimization of extraction and elution cycles

A central composite design was performed to optimize the extraction and desorption cycles as well as the percentage of salt to be added. The number of cycles can influence on the efficiency in which the analytes are desorbed from the extraction phase to the desorption solvent. This step is important to ensure that no carryover effect hinders the analytical procedure. In this evaluation, the chromatographic responses were monitored with the application of 1 to 11 desorption cycles using the previously optimized conditions. Six cycles were enough to achieve the highest desorption efficiency. Figure 5 shows the peak areas increase when cycles from 1 to 5 are evaluated. The result can be related to the unreached sorption equilibrium.¹⁹ From 7 to 11 desorption cycles, the peak areas decreased possibly due to a decrease of the solvent extractive efficiency. Since the same aliquot is used during the desorption procedure, as more cycles was used (from 7 to 11) it is likely that a re-adsorption of part of the analytes is occurring. Six desorption cycles were chosen as optimized condition.

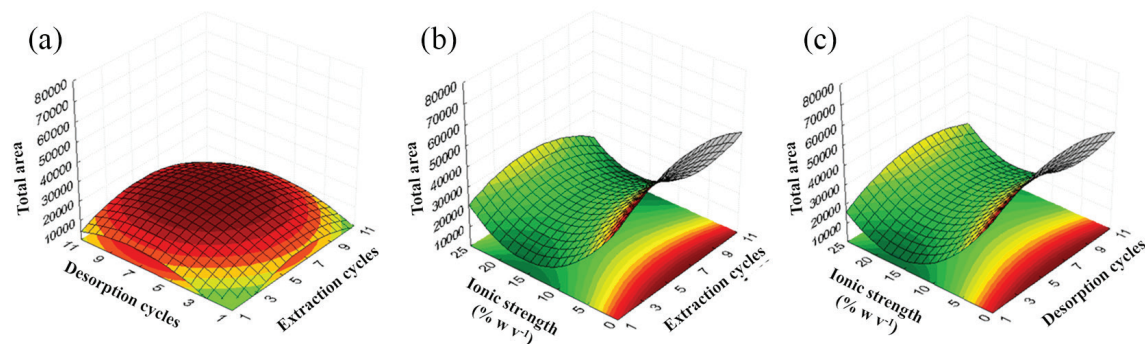


Figure 5. Optimization of the extraction and desorption conditions through a central composite design. Response surface shown in (a) represent the optimization of the extraction step and the optimization of the desorption step and the response surfaces shown in (b) and (c) represent the optimization of the effect of adding salt. Experimental conditions: 700 μL of ultrapure water spiked with 5 $\mu\text{g L}^{-1}$ of 4-methylthiophene, cycles of 30 s for the extraction, 20 mg of 8-HQ immobilized with Pd^{II} as sorbent phase, desorption with 200 μL of methanol, desorption cycles of 30 s.

In many cases, the addition of NaCl causes the salting out effect, reducing the solubility of the analytes in the water, thus facilitating their extraction.^{28,36} The effect of salt addition on the extraction efficiency was evaluated varying the amount of sodium chloride from 0 to 25% (m v^{-1}). Figure 5 shows the negative effect of the presence of salt on the extraction and desorption efficiencies and the best analytical response was obtained without NaCl. Studies by Yu *et al.*¹⁴ also showed a negative effect of NaCl on the extraction procedure, corroborating our results, probably due to the relatively low polarity presented by the PASHs.

The experiment was carried out with one analyte to evaluate the number of extraction and desorption cycles. Subsequent tests including all analytes were performed in order to verify possible interferences during the adsorption (competition between the analytes). The results of the DPX extraction indicated that the analytes were adsorbed/desorbed with no interference of one with other. A schematic representation of the overall process of DPX is demonstrated in Figure 6.

Analytical parameters and application

Table 1 shows the analytical parameters obtained for the optimized conditions of the method using the analytical curve constructed using lagoon water samples, ranging from 10-100 $\mu\text{g L}^{-1}$ with determination coefficients higher than 0.9711 for external standard analytical curves, and higher than 0.9729 for analytical curves prepared spiking standards in the leachate (Figure 1). Based on the analytical curves with lagoon water, the limits of detection (LOD) and quantification (LOQ) for the PASHs were found to vary between 1.0 and 2.9 $\mu\text{g L}^{-1}$ and 3.1 and 8.8 $\mu\text{g L}^{-1}$, respectively, whereas for the PASHs in the leachate LOD and LOQ extended from 0.1 to 2.5 $\mu\text{g L}^{-1}$ and from 0.2 to 2.7 $\mu\text{g L}^{-1}$, respectively. Differences in the LOD and LOQ values are due to the matrix effect caused by the suspended particulate material found in the lagoon water samples. The linear range is in accordance with the limit values proposed by the ABNT NBR 10004/2004¹⁶ for PAHs.

The precision and the accuracy of the method were evaluated using lagoon water samples collected from the

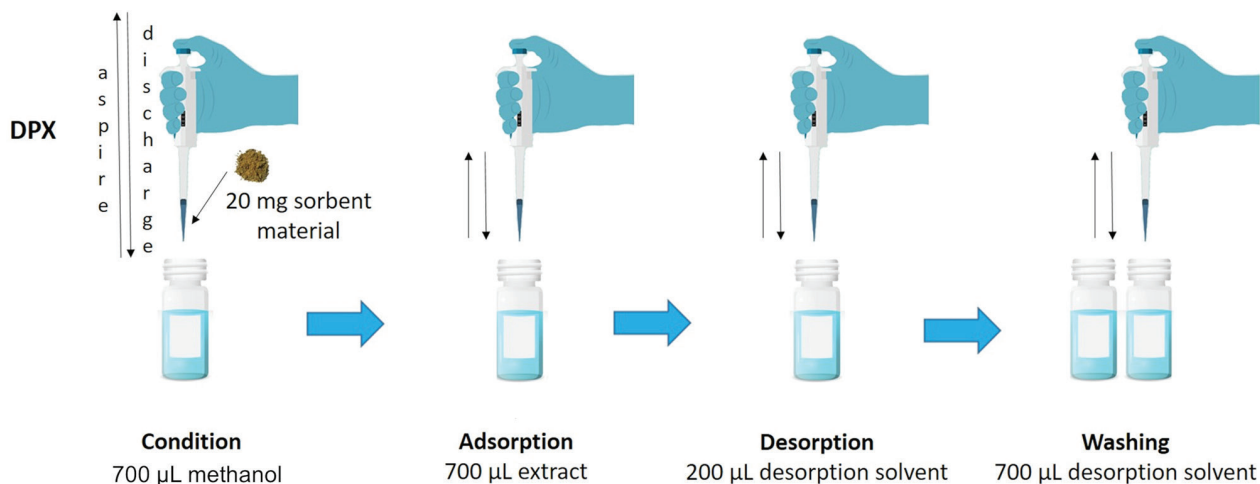


Figure 6. Schematic representation of the overall DPX process.

Table 1. Analytical method parameters obtained for the proposed method for the determination of PASH in water samples and leachate solid waste by DPX allied to GC-MS

Analyte	Linear range / ($\mu\text{g L}^{-1}$)	R^2		LOD / ($\mu\text{g L}^{-1}$)		LOQ / ($\mu\text{g L}^{-1}$)		Spiked concentration / ($\mu\text{g L}^{-1}$)		Precision (n = 3)		Recovery ^c / %	
										(RSD) / %			
2-Methylbenzothiophene	10-100	0.9945 ^a	0.9742 ^b	1.3 ^a	0.9 ^b	4.0 ^a	2.7 ^b	10.0	7.6 ^a	19.4 ^b	114.1 ± 9.9 ^a	113.5 ± 22.8 ^b	
								50.0	4.7 ^a	7.3 ^b	124.2 ± 11.6 ^a	72.7 ± 8.8 ^b	
3-Methylbenzothiophene	10-100	0.9955 ^a	0.9935 ^b	1.0 ^a	0.1 ^b	3.1 ^a	0.3 ^b	10.0	1.6 ^a	12.9 ^b	74.6 ± 13.3 ^a	105.0 ± 4.0 ^b	
								50.0	3.2 ^a	1.8 ^b	102.1 ± 13.1 ^a	90.6 ± 1.9 ^b	
4-Methylidibenzothiophene	10-100	0.9964 ^a	0.9913 ^b	2.9 ^a	0.1 ^b	8.8 ^a	0.2 ^b	10.0	3.7 ^a	6.1 ^b	121.3 ± 3.3 ^a	100.0 ± 1.1 ^b	
								50.0	0.7 ^a	1.5 ^b	114.2 ± 19.3 ^a	86.7 ± 1.9 ^b	
4,6-Dimethylidibenzothiophene	10-100	0.9782 ^a	0.9798 ^b	2.1 ^a	0.3 ^b	6.3 ^a	0.9 ^b	10.0	1.3 ^a	11.5 ^b	131.2 ± 2.1 ^a	118.0 ± 2.4 ^b	
								50.0	9.1 ^a	5.9 ^b	115.6 ± 8.1 ^a	77.6 ± 5.9 ^b	
1,2-Naphthobenzothiophene	10-100	0.9711 ^a	0.9729 ^b	2.4 ^a	2.5 ^b	7.4 ^a	7.7 ^b	10.0	9.2 ^a	13.9 ^b	127.3 ± 5.7 ^a	100.0 ± 5.4 ^b	
								50.0	0.3 ^a	3.8 ^b	78.3 ± 0.2 ^a	93.4 ± 4.1 ^b	

^aIn water sample; ^bin the leachate of the solid waste; ^cPASH recovery ± standard deviation (n = 3); LOD: limits of detection; LOQ: limits of quantification; RSD: relative standard deviation.

Patos Lagoon, Rio Grande do Sul, Brazil, and leached extract from solid waste samples provided from a petroleum hydroprocessing unit. In this procedure, the samples were spiked with the PASH standards at two different concentration levels (10.0 and 50.0 $\mu\text{g L}^{-1}$). In order to determine the intra-day precision of the method, triplicate analyses of three independent samples were performed at these two concentration levels, resulting in relative standard deviation (RSD) values between 0.3 and 9.2% for the lagoon water samples and 3.8 to 19.4% in the leachate of the solid waste samples.

The accuracy of the method was estimated based on the mean recovery of the analytes in the spiked samples. On average, the recoveries were satisfactory for water samples (between 74.6 and 131.2%) and for leachate of the solid waste samples (72.7 and 118.0%). The high recovery values observed in the lagoon water samples can be attributed to the presence of suspended material, resulting in matrix effects. However, for the leachate extract the current method demonstrates high selectivity for the PASHs since other organic constituents usually found can be coextracted for the classification of the petrochemical residue.

The DPX performance using 8-HQ-Pd silica gel was compared to the results obtained with two other sorbents (silica gel and C_{18}) under the same optimized conditions. The total amount of analyte extracted with 8-HQ-Pd silica gel was higher compared with C_{18} and silica gel, by factors of two and seven, respectively.

Gimeno *et al.*¹³ have reported the separation of PASH and PAH in seawater and sediment samples using high-performance liquid chromatography with fluorescence and atmospheric pressure chemical ionization with mass

spectrometry detection obtaining much lower LOD. However, in their study no isomers were used as analytes and had very distinct molecular masses, making the separation more efficient with no co-elution. A similar study has been reported by Yu *et al.*¹⁴ using HPLC for the determination PASHs and PAHs in lake water and soil samples, where no isomeric compounds were analyzed.

In this study, the use of 8-HQ-Pd silica gel has the advantage of eliminating parental PAH and their alkylated derivatives during the extraction by DPX allowing the analysis of PASH without interferences. The sorption step aims to minimize interferences and is usually performed with stationary phases containing metals like Pd^{II} that shows great affinity with sulfur. Metals can be physically adsorbed^{15,37} or coordinated to chelating groups of organofunctionalized silica surfaces. The most used metal in a ligand exchange chromatography is Pd^{II}, because it is considered more selective and efficient for organic sulfur compounds.^{7,8,15,38}

The performance of DPX using 8-HQ-Pd silica gel was evaluated in the presence of a mixture of 16 HPAs with concentration of 100 $\mu\text{g L}^{-1}$. The results indicated no interference of the PAH in the determination of the PASHs. Compared to other methods, the present study has the advantage of using less than 2 mL of solvent and is performed in only one step, making it an environmentally-friendly alternative for sample preparation. In addition, with less manipulation of the sample, the method allows reduced exposure to contaminated samples, decreasing the health risks for the analyst.^{13,14}

The method has been applied to four samples of surface water collected in a lagoon near a marina and to three samples of solid waste from a petroleum

hydroprocessing unit. Several PAH were found in the leachate from the petroleum residues and three PASHs, 3-methylbenzothiophene, 4-methylbenzothiophene and 4,6-dimethyldibenzothiophene were detected above the LOD. A great number of organic compounds can be present in hazardous solid wastes generated in the petrochemical industry. They can be formed during the petroleum cracking process. Thus, considering that these petrochemical residues are a good source of energy and are often incinerated, the determination of PASHs in the leachate solid waste is of great importance and should be part of the regulatory requirements. In the water analysis of the lagoon two PASH (3-methylbenzothiophene and 2-methylbenzothiophene) were found in all the samples collected with concentrations between LOD and LOQ values. The presence of PASHs may be associated with the type of fuel usually employed in the engines of the boats.

Difficulties to separate PASHs from PAHs are reported due to their similarity in structure and coelution problems during chromatographic analysis.^{3,7,10,33} The results achieved with the proposed methodology demonstrated that DPX can be selective to PASHs applied to real samples even in the presence of other organic compounds. In addition, it has a low cost with less sample preparation time and amount solvent compared to other analytical methods for the determination of PASHs in aqueous matrix^{13,14} and crude oil samples.^{3,7,10,15}

Conclusions

In this study, 8-HQ-Pd silica gel was used as an alternative sorbent for the DPX technique. The procedure provides good results when the microextraction technique is applied in the detection of low concentrations of PASHs in aqueous samples and solid waste. The methodology developed was tested on real water samples collected at the Patos Lagoon, Rio Grande do Sul, Brazil and leachate of solid waste samples provided from a petroleum hydroprocessing unit. DPX offers more versatile approaches to analyte enrichment and simultaneous clean-up. The procedure is easy to use and involves less work and less time than the classical methods. In summary, DPX is a simple, rapid and inexpensive sample preparation technique, which represents a promising procedure for the separation and identification of PASHs in water samples from distinct matrices.

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbq.org.br> as PDF file.

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Author Contributions

Karine O. Garcia was responsible for conceptualization, data curation, formal analysis, investigation methodology, validation, visualization and writing original draft; Morgana Frena for conceptualization and writing-review and editing; Otávio R. Bittencourt for methodology, resources and writing-review and editing; Hérica A. Magosso for methodology and resources; Eduardo Carasek for resources, supervision and writing-review and editing; Luiz A. S. Madureira for funding acquisition, project administration, resources, supervision and writing-review and editing.

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