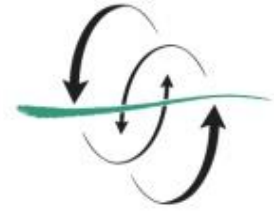


FACULTAD
DE CIENCIAS
DEL MAR



UNIVERSIDAD DE LAS PALMAS
DE GRAN CANARIA

**Extraction system and
determination of PAH in
seawater and its
implementation in
submarine vehicles.**

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Sistemas de extracción y determinación de hidrocarburos en agua de mar y su acoplamiento en vehículos submarinos

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are a potential risk for human health and marine biota in general that make necessary the monitorization of them. A miniaturized extraction system capable to extract PAHs from seawater was developed and optimized with the objective of implement it in an oceanographic buoy in the future. An analytical method was optimized by high performance liquid chromatography (HPLC) for the determination of extracted PAHs by the extraction system. The analytical method was validated and applied to real samples of different points of Gran Canaria. The method has enough sensitivity to detect and quantify concentrations below the concentrations established in the legislation. In some places where samples were taken some compounds exceed the legislation while other compounds follow it.

The results obtained in this work and included in this TFT will be sent for its publication in the "Analytica Chimica Acta" magazine, the first quartile in the area of analytical chemistry.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAH) are compounds formed by two or more aromatic rings in different arrangements [1]. They are considered ubiquitous compounds due to their persistence in the environment and they have several degrees of toxicity and persistence [2]. It has demonstrated that some of these compounds have carcinogenic, mutagenic and/ or teratogenic properties and constitute a potential risk for human health [3][4]. For this reason it is very important to control and monitorize them. To facilitate this labor the United States Environmental Protection Agency (USEPA) has elaborated a list in which 16 PAHs of most interest due to their toxicity and dangerous were listed. The European Commission has regulated the monitorization of these compounds through the Water framework directive (2000/60/CE). This directive has been modified and this modification can be found in the directive (2008/105/CE) which regulates the environment quality norms for dangerous priority substances and other contaminants [5]. In this directive are listed 5 PAHs as dangerous priority substances. These are benzo[a]pyrene, benzo[b]fluorene, benzo[g,h,i]perylene, benzo[k]fluoranthene, indene[1,2,3-cd]pyrene.

The two main properties of PAHs are their hydrophobic character and their low vapor pressure. These two properties vary with the molecular weight of the compound being more apolar compounds of high molecular weight and more volatile compounds of low molecular weight [1]. These properties control the presence and distribution of PAHs in the marine environment. When hydrophobic character increase the trend of compounds to adsorb onto particles also increase [3]. Each compound presents a characteristic absorption spectrum. This property facilitates the identification of each compound. The wavelength of the absorption increases with the number of aromatic rings of the compound [6]. Many PAHs have fluorescence and this permit determine them with more sensitivity and selectivity [2].

They can be produced and released to the environment by natural or anthropogenic sources. PAHs present several origins, although the two main are petrogenic and pyrogenic origin. Pyrogenic PAHs present high molecular weight than petrogenic PAHs [7][8]. Several ratios are been used in function of analyzed compounds to determine their origin [3][9][10]. The 16 PAHs of the USEPA can be classified as low molecular weight PAHs (2 to 3 rings) that include naphthalene, acenaphthylene, fluorene, acenaphthene, phenanthrene and anthracene. As high molecular weight PAHs (4 to 6 rings) the classify includes fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b] fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indene[1,2,3-c,d]pyrene, benzo[g,h,i]perylene and dibenz[a,h]anthracene. Some of compounds used in this study are included in the figure 1.

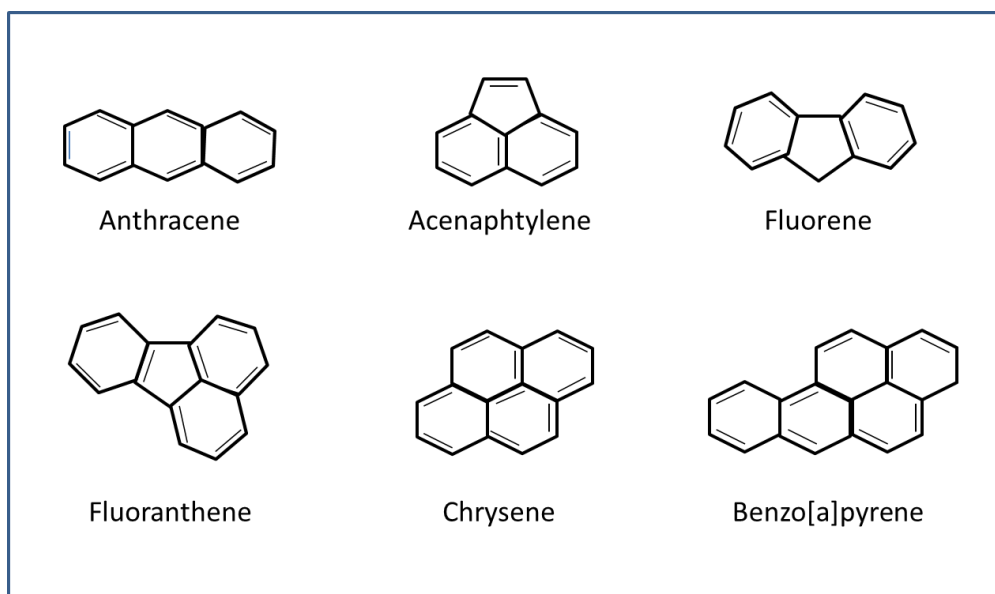


Figure 1: Some PAHs included in the USEPA list and used in this study.

In the marine environment the main inputs of PAHs are atmospheric, rivers, ports and waste waters ways [2][10]. The concentration of these compounds is higher in coast water than in the open ocean. The distribution of PAHs depends to the properties cited previously [3]. A positive correlation between the different PAHs of high molecular weight and the amount of total organic carbon (TOC) in sediment samples has been observed [11]. This fact suggests an enrichment of these compounds in the sediment zone and due to the dynamic of these contaminants this zone can become a contaminant reservoir. However, low molecular weight PAHs are more abundant in superficial waters due to inputs by different ways, especially in the superficial microlayer where the concentration of PAHs are higher than the waters below [12]. The half-life period of low molecular weight PAHs is reduced in the water column due to the degradation. This cause the limitation of low molecular weight PAHs transport to deep waters [3]. Process and fates of some PAHs are shown in the figure 2.

The accumulation of these contaminants is facilitated due to their hydrophobic character. For this reason this property is related with the bioaccumulation, bioconcentration and biomagnification factors in organisms. High molecular weight PAHs are considered genotoxic due to they can be bioactivated after the biotransformation and generate electrophilic derivate which can react with the DNA chain and produce damage in it [1][13]. The adsorption of these compounds to

multiple surfaces increase the bioavailable in the marine environment and producing the introduction of PAHs in the food chain [9][11].

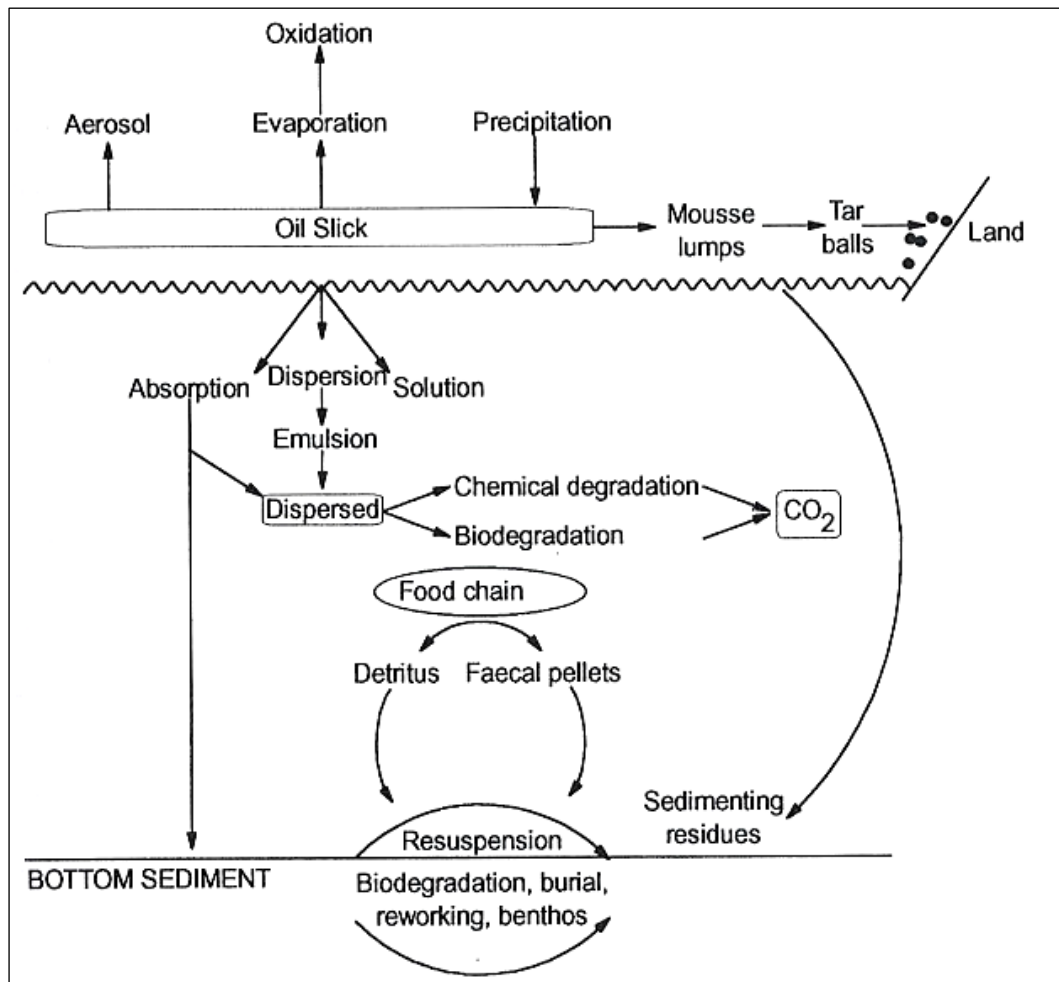


Figure 2: Process and fate of petrogenic PAHs in this case. Extracted and modified from [14].

In the marine environment the main exposure route is through the gills or the aliment. The concentration of contaminants in organism depends to the metabolism of it [1][11]. Invertebrates lack of an efficient mechanism to remove PAHs from their organism producing bioaccumulation into them. Some of them such as bivalves mollusks are used to monitorize these contaminants in the marine environment in projects such as the Biological effects of environmental pollution in marine coastal systems: European programme (BIOMAR) [9].

The most used analytical techniques for determination of these compounds are the Gas Chromatography (GC) or the High Performance Liquid Chromatography (HPLC) [15]. By HPLC several isomers of different PAHs can be separated and need not a previous clean-up for analysis [16][17]. Different methods of detection can be used with these two techniques. For HPLC the most used are UV-visible and fluorescence detection. The fluorescence method provides higher selectivity and sensitivity than the UV-visible method [6].

An extraction and preconcentration step previous to the analysis is needed due to the very low concentration of PAHs in seawater. In the case of seawater the salinity and the presence of fulvic and humic acid affect the adsorption of these compounds to the particulate phase. For this reason seawater should be prefiltered before the preconcentration step [6]. There are several methods of preconcentration such as liquid-liquid extraction (LLE), solid phase extraction (SPE), supercritical fluid extraction (SFE) and (SPE/SFE). The SPE obtains better results than the others [16]. Currently this technique is usually used due to its higher advantages such as the use of small volumes of organic solvent, diminish the time of the preconcentration and the high availability of sorbents in the market that help to the optimization of the process and the reduce of costs [16]. For this study the SPE method has been selected for the extraction and preconcentration step but with a modification and a miniaturization. For the optimization of the method is necessary the study of the conditions of the extraction such as the composition of the fill, the volume of the sample and the amount of solid sorbent used [16].

The extraction and monitorization of these compounds is one of the objectives of this study to medium term and the optimization of the extraction is a critical step for carry out it. Currently, several experiences exist for monitorization of PAHs using optic sensors coupled to AUV but not for take samples in situ for its posterior analysis in laboratories. The Monterey Bay Aquarium Research Institute (MBARI) deployed an AUV to characterize the deep plume of oil spill during the disaster of the Deepwater Horizon to improve the understanding of this phenomenon. As a result a persistent plume was obtained and related with the origin of the spill [18][20]. Recently, fluorescence sensors are beginning to be used, for example in (S. Jocis and F. Pierce) some of them are tested for couple anyone to a Bluefin spray glider [18]. Other systems used are the autosamplers. These systems consist in a silicon rubber surface coated by a semipermeable membrane by which contaminants present affinity. An application of this sampler can be seen in (L. Suberg et al. 2014) [21].

The main objective of this work is the extraction of PAHs from seawater by active systems for its posterior analysis by HPLC. The extraction has been realized by the optimization of a miniaturized SPE system as a basis for future studies that allow the automatization and coupled to a submarine vehicle or an oceanographic buoy.

2. Material and methods

2.1 Elaboration of the standards

The compounds used as standards were acenaphthylene (Acen), fluorene (Flren), phenanthrene (Phe), anthracene (Anth), fluoranthene (Flran), benzo(a)anthracene-7,12-dione (B(a)an), chrysene (Chry) y benzo(b)fluoranthene (B(b)flu) purchased in Sigma-Aldrich® and benzo(a)pyrene (B(a)pyr) from Supelco®. These compounds were diluted in acetonitrile in concentrations among 700 and 1000 ppm attending to their maximum solubility value in the dissolvent.

An individual secondary standard of 2ppm was prepared for each compound with methanol. The simultaneous analysis for all compounds was carried out with a tertiary standard of 0.5 ppm in methanol. The reagents used as methanol and acetonitrile were of Panreac® HPLC gradient quality.

2.2 Preparation of samples

The seawater that was used for the optimization was collected directly from a water intake in the installations of the Plataforma Oceánica de Canarias (PLOCAN) with a previous filtered step. Seawater was collected every day during the period of the optimization and the validation of the method. Seawater was filtered with a glass fiber filter Whatman® GF/C (porosity of 1.2 µm) before the spike of the sample for the optimization and the extraction method. The spike was realized to 5, 3, 1 and 0.1 ppb of concentration in the seawater. These standards were made with Mili-Q water as solvent.

2.3 Instrumentation

The active extraction system includes a peristaltic pump of ISMATEC® trade mark, model: ISM 846, with connectors of SKALAR® trade mark, model: 3091 for each channel of the pump. The miniaturized SPE extraction system was connected to a neoprene tube of 4.8 mm of diameter as is detailed in the section 2.5.

For the determination of PAHs a HPLC VARIAN[®] Pro Star, model 230 chromatograph was used with a PDA (photo-diode array) model 335 and a fluorescence detector 363 both VARIAN[®] Pro Star. Finally a VARIAN[®] Column valve module, model 500 with a VARIAN[®] HPLC Column 150x4.6mmx1/4", Microsorb-MV 100-5 C18 were used.

2.4 Chromatographic Analysis

The column was kept up about 30°C during all the analysis. The mobile phases consisted in a mobile phase A compound by a mixture of methanol and Mili-Q water in a proportion of 80:20 and a mobile phase B with 100% of methanol. The method consisted in a gradient of both mobile phases along the time with a flow of 1.00 ml/min as is represent in the figure 3. The PAHs were determined at a wavelength of 254 nm for the UV detector. For fluorescence detection the wavelengths of excitation and emission were between 280 and 315 nm and between 340 and 410 nm respectively [19].

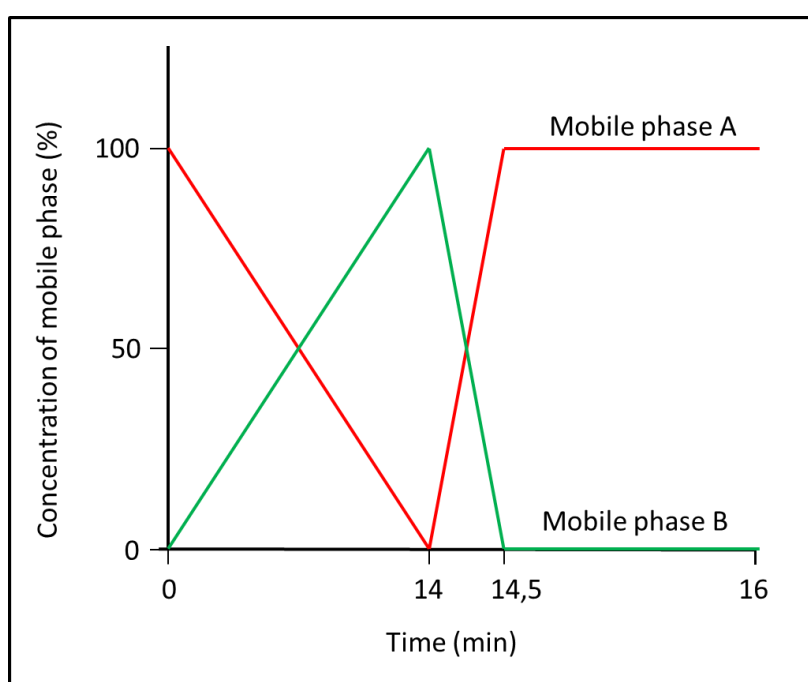


Figure 3: Chromatographic method used for the determination of PAHs, in gradient modality.

Compound	Retention time (min)
Acen	4,75
Flren	6,51
Phe	6,75
Anth	7,06
Fran	8,29
B(a)an	9,08
Chry	10,65
B(b)flu	12,99
B(a)pyr	13,83

Table 1: Retention time of each compound

2.5 Preparation of extraction system and its optimization

The extraction system consists in a neoprene tube (TYGON®, SC0359) with an internal diameter of 4,8 mm and a length of about 9,2 cm. For fill the content of several models and trademarks of SPE cartridges were used. The SPE cartridges used were ENVI-18 from Supelco®, Hypersep SCX from THERMO® scientific and the UPTI-CLEAN from Interchim®. Finally, in both extremes a joint (IDEX®, ISM560) for a tube of 5 mm was used and in the internal part of joints an adapted fragment of a Frit was disposed. This Frit is made of polyethylene (Sigma-Aldrich®, 57183 Supelco) and has a porosity of 20µm. The figure 4 shows all of these components and a prepared extraction system.

For optimization of the extraction system the composition of the fill was varied with different SPE cartridges and the weight of the fill for 0,5, 0,4 and 0,3 g. The preconcentration step was carried out with 1 liter of prefiltered seawater with a spike of 5 ppb of concentration. The best extraction system was selected, the spike was varied to 3, 1 and 0,5 ppb and the weight was varied for 0,1 and 0,2 g. When the optimization was finalized the validation of the method, the reproducibility and the limit of detection was done.



Figure 4: Example of used extraction system, including the internal components added.

2.6 Summary of the procedure of extraction and determination (Figure 5)

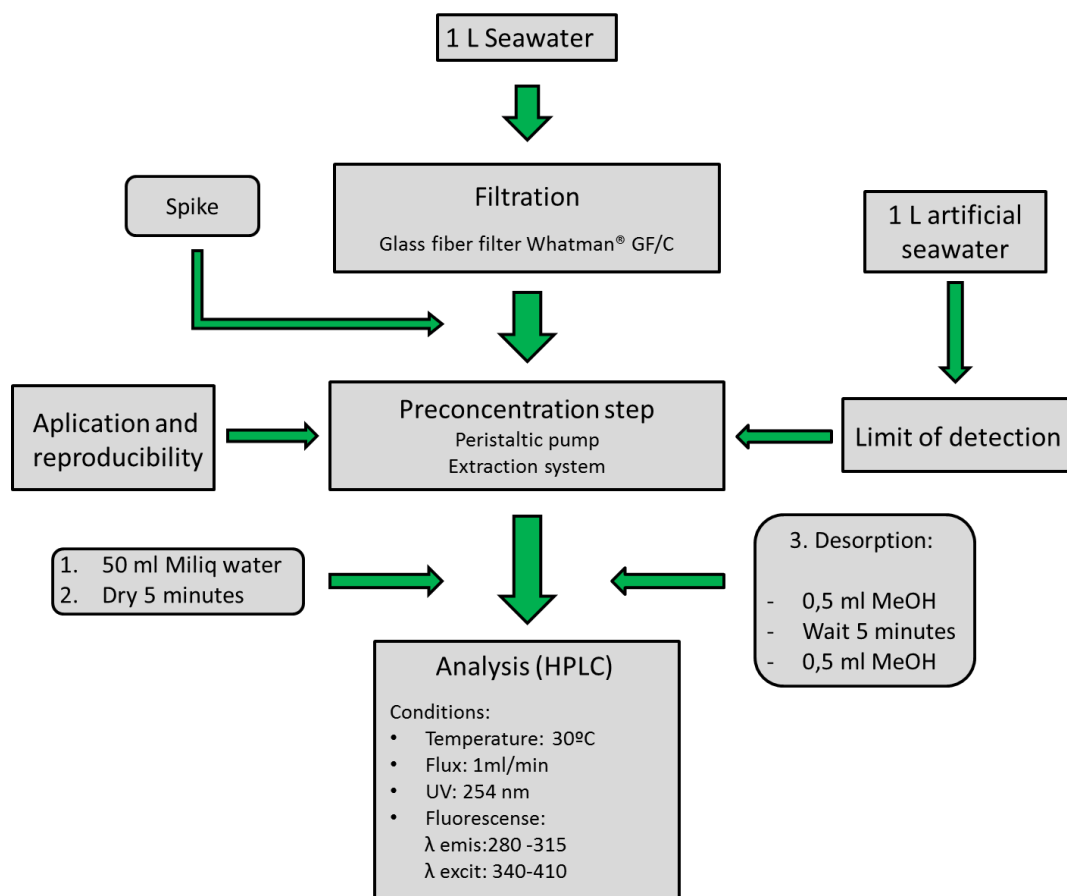


Figure 5: Flux diagram of the carried out procedure.

3. Results

3.1 Preselection of solid sorbent (SPE)

The preselection of the optimum sorbent for our study was the first step for optimization of the extraction system. The recoveries obtained for the 9 studied PAHs were checked after passed seawater through the extraction system while the composition of the fill and the weight of sorbent was varying. Results are shown in the figures 6 and 7.

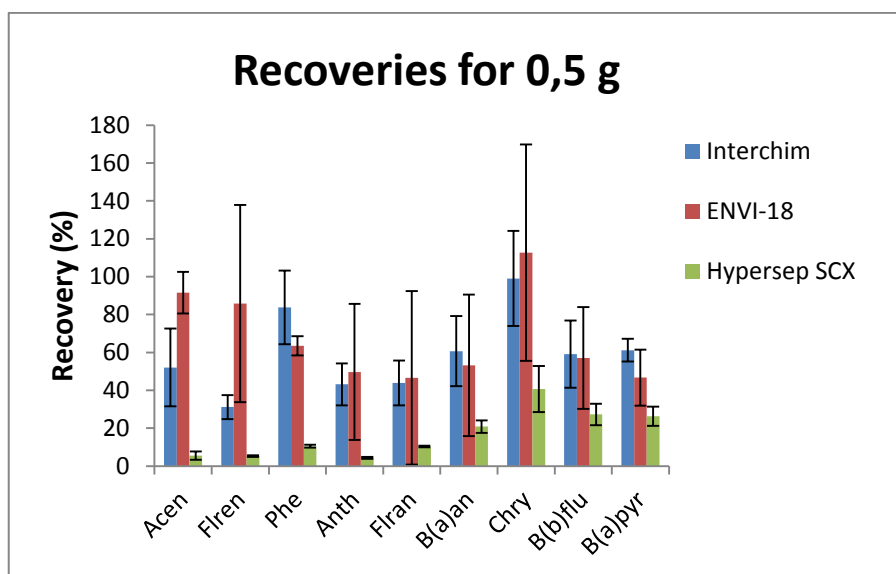


Figure 6: Recoveries for 0,5 grams using three different solid sorbents.

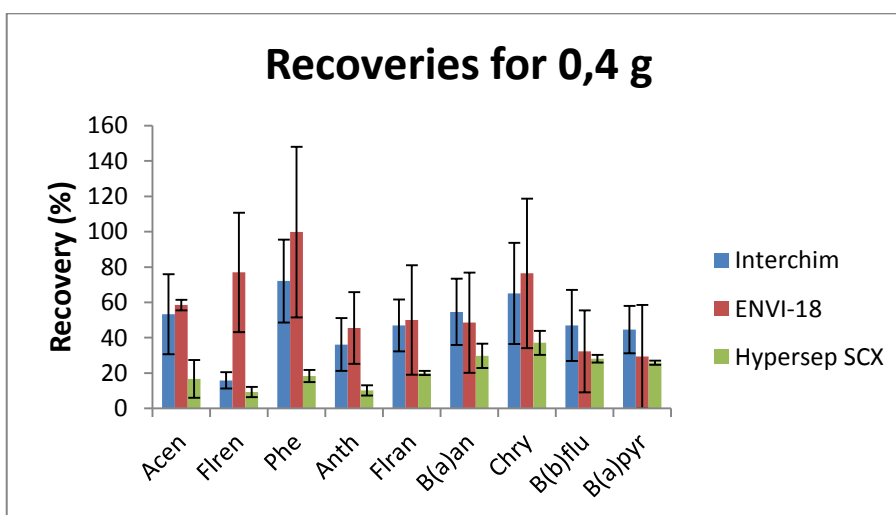


Figure 7: Recoveries for 0,4 grams using three different solid sorbents

The best recoveries were observed for the extraction systems which used SPE sorbent of ENVI-18 and Interchim composition for the two weights used. The Hypersep SCX

composition was discarded for next phases of the study due to the low recoveries of it. Then, the two extraction systems were compared again with a reduction of the weight of sorbent. Results are shown in the figure 8.

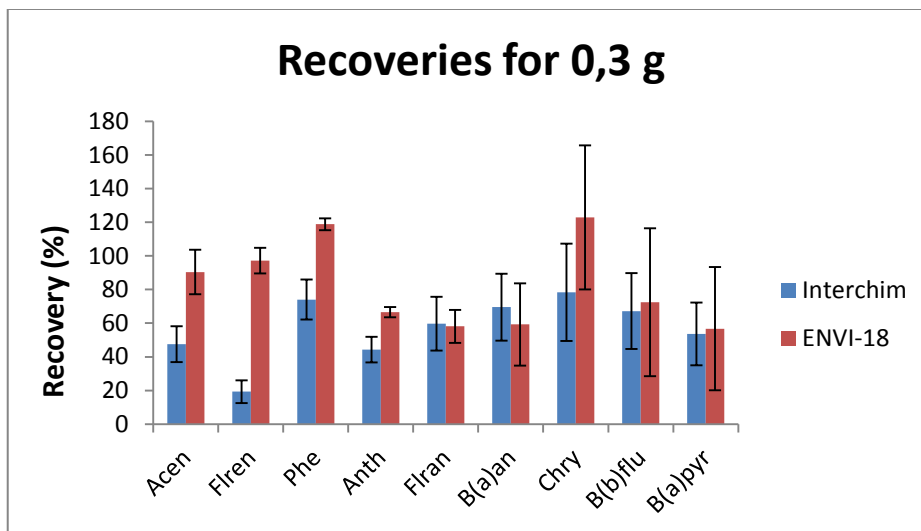


Figure 8: Recoveries for 0,3 g using two different solid sorbents

In general, it was observed that the composition with the best recoveries was for ENVI-18 and therefore this was the composition selected for rest of the optimization. Weights were compared too and the 0,3 g was selected as a weight of SPE sorbent. Results are shown in the figure 9.

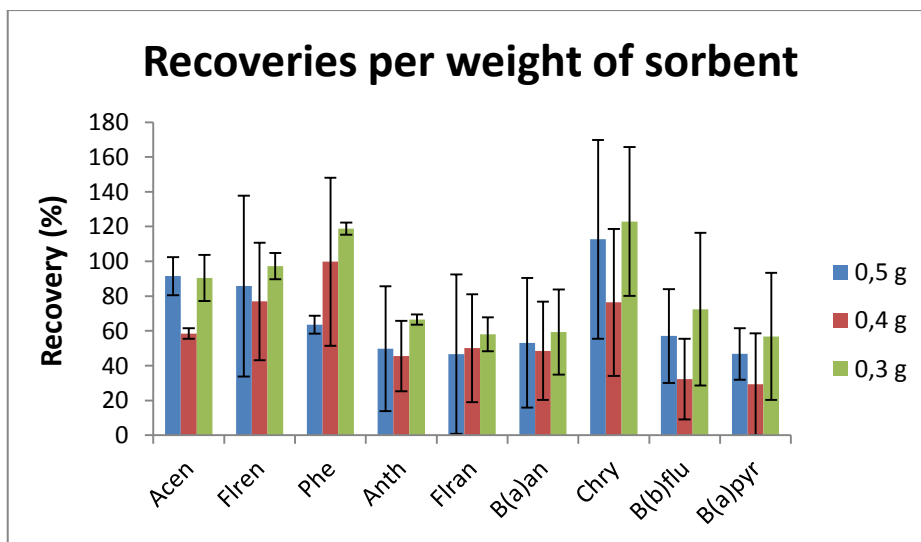


Figure 9: Recoveries for different weights of sorbent.

3.2 Optimization of the extraction system.

With the optimized weight the validity for several concentrations was tested using 1 liter of sample as a reference value. This step allowed tested the efficiency of the extraction system for low concentrations and it was observed some lost for this concentrations (Figure 10). For rest of the optimization an intermediate sample of 1 ppb in seawater was chosen to guarantee the quantification of the nine compounds above of the minimum levels (LOQ)

With a little differences especially for some of the most apolar compounds the most efficient weight for 1 liter of sample was 0,3 g. This presents higher recoveries for the low molecular weight PAHs which are abundant in the superficial waters. If the volume of the sample would be increased for the detection of lower concentrations, a test would be necessary to determine if the weight is the optimum. In this way the viability of the miniaturization of a SPE system portable and automatable is confirmed. This fact is especially interesting for a future couple to a submarine vehicle or an oceanographic buoy which will be established in the environmental control zones.

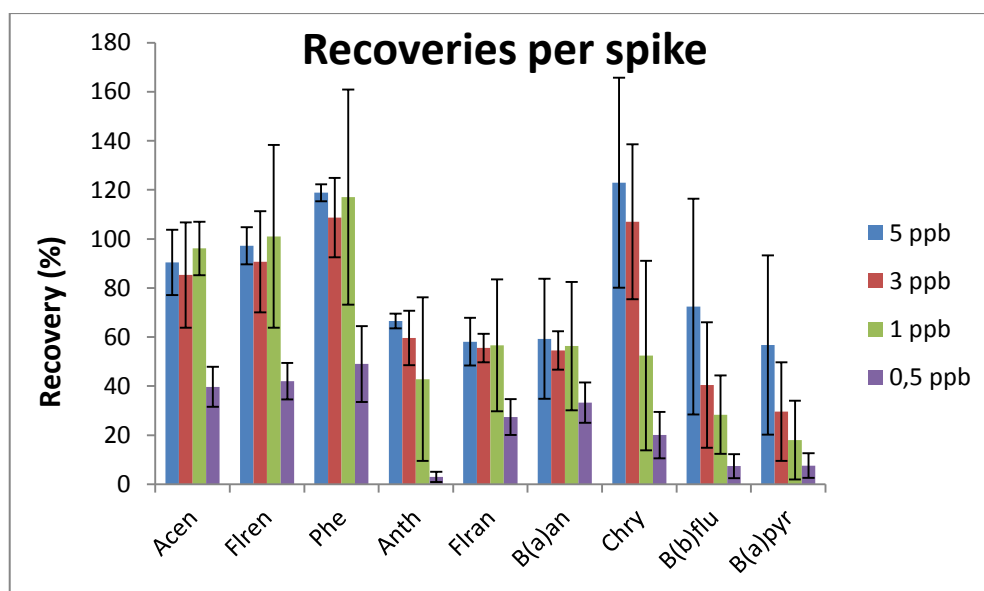


Figure 10: Recoveries per spike.

Finally, for tested if the efficiency increased or diminished with a diminution of the weight this was tested again. These recoveries vary for polar and apolar compounds but the weight of sorbent of 0,3 g was selected. Results are shown in figure 11.

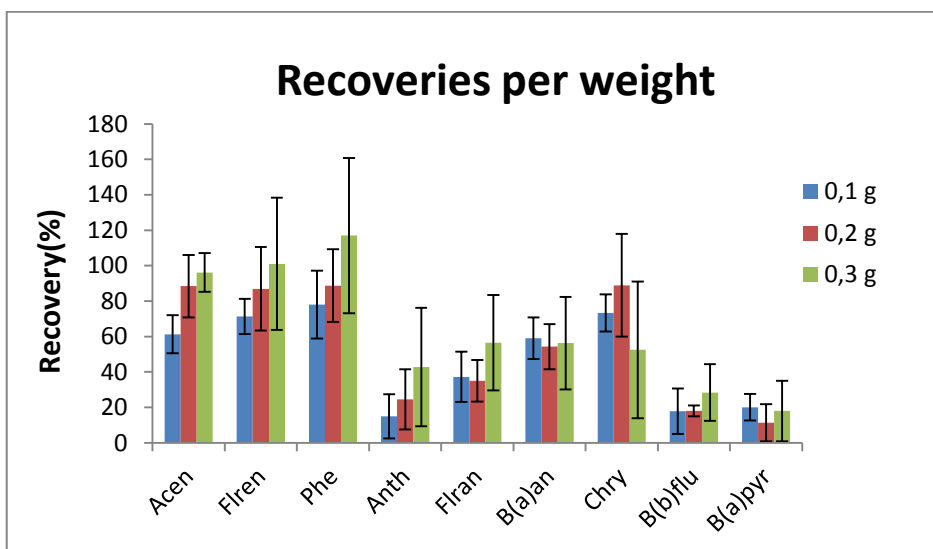


Figure 11: Recoveries for the optimization of the weight.

3.3 Limit of detection and reproducibility.

The limit of detection was realized two times with artificial seawater. The reproducibility was carried out 7 times with prefiltered seawater and with a spike of a known concentration of 1 ppb. For the reproducibility and the limit of detection the procedure detailed in the section 2.2 was carried out.

The concentration of compounds detected in the artificial seawater (control) was calculated for the limit of detection and the limit of quantification. This value was multiplied by 3 for the limit of detection and by 10 for the limit of quantification. Finally, units were converted to ppb ($\mu\text{g/L}$). The reproducibility was calculated with a mean of tests. Results are shown in the table 2.

Compound	% RSD	LOD ($\mu\text{g/L}$)	LOQ ($\mu\text{g/L}$)
Acen	3,07	2,64	8,81
Flren	5,20	0,07	0,23
Phe	7,25	0,12	0,40
Anth	10,23	0,12	0,42
Flran	3,76	0,02	0,06
B(a)an	11,90	0,06	0,18
Chry	12,84	0,02	0,07
B(b)flu	3,84	0,02	0,05
B(a)pyr	6,06	0,04	0,12

Table 2: The table shows the limit of detection (LOD), limit of quantification (LOQ) and the relative standard deviation (% RSD).

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The %RSD is below of 10% in most cases with a little differences for chrysene, benzo(b)fluoranthene and anthracene due to their apolar character that make these compounds have low affinity for seawater and tend to adsorb into any surface of the instrumentation. For the limit of detection and the limit of quantification the only compound that presents a limitation in the detection is the acenaphtylene.

3.4 Applications

The samples for applications were taken in the places cited in table 2 and shown in figure 12. The seawater was stored in a glass recipient and conserved about 4°C until its posterior analysis. The analysis was realized two times following the procedure detailed in the section 2.6 but without addition of PAHs through the spike.

Site of sample	Latitude and Longitude
A. Seawater intake of Taliarte (Telde)	27°59'27,49" N
	15°22'02,57" O
B. Playa de alcaravaneras (Las Palmas de Gran Canaria)	28°07'36,77" N
	15°25'31,19" O
C. Puerto de las nieves (Agaete)	28°06'01,55" N
	15°42'45,89" O
D. Muelle deportivo (Las Palmas de Gran Canaria)	28°07'36,77" N
	15°25'31,19" O
E. Muelle de Taliarte (Telde)	27°59'22,81" N
	15°22'07,22" O

Table 2: Sites of sample.

The results of the applications are shown in the figure 13. In general, low molecular weight PAHs were detected in higher concentrations than the others. High molecular weight PAHs were detected at low concentrations, this is due to their hydrophobic character that makes these compounds adsorb into the particles and accumulate in sediments. As it is shown in figure 13 the Puerto de Las Nieves (Agaete) present the highest concentration for all compounds that were detected except for anthracene. This can be due to the release of these compounds by boats of this port and by maintenance labors of the ferry of Fred Olsen Company. The quiet of these waters facilitate accumulation of these compounds in the port waters. The Muelle Deportivo presents a similar pattern but with lower concentrations than Puerto de Las Nieves (Agaete). For other places, compounds were detected at low concentrations except for anthracene that present a high concentration for all the places.

The best concentration for this compound was the seawater intake in the installations of PLOCAN.



Figure 12: Localization of samples sites.

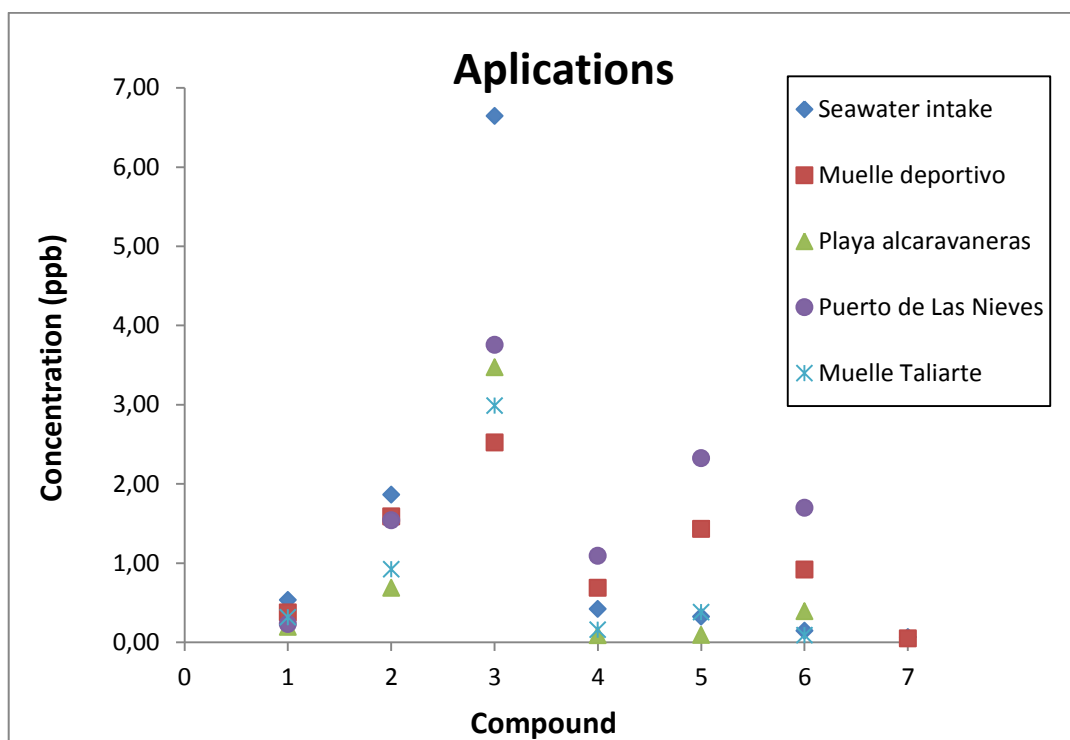


Figure 13: Applications of the extraction system. The compounds represented are: 1- Fluorene, 2-Phenantrene, 3-Anthracene, 4-Fluoranthene, 5-Benzo(a)anthracene, 6-Chrysene, 7-Benzo(b)fluoranthene.

4. Discussion

A new miniaturized and portable extraction system of contaminants from seawater was developed. It has been validated for the detection of PAH in seawater for different points of Gran Canaria coast.

Recoveries are not high (below of 50% in some cases) for the most apolar compounds. This is due to their hydrophobicity and the adsorption of them onto the surface of the instrumentation. Even so a detectable levels below the concentration established in the legislation were observed.

For the most polar compounds it can be observed values of recovery up to 120% in some cases. This is due to the used seawater for the optimization that was contaminated with PAHs. Therefore this contamination makes that the known concentration of the added spike was exceeded even subtracting the control to obtained recoveries. This is due to a residual concentration below of the limit of detection. For minimize a residual retentions of analytes in the extraction system, the variability in function of the composition of the tubes will be study in the future.

In the results a general trend between the recovery and the molecular weight was observed for each compound. High molecular weight PAHs were recoveries at lower concentrations than low molecular weight PAHs. This is due to the hydrophobic character of the first that make these PAHs adsorb onto any surface of the instrumental used in the process.

The limit of detection and the limit of quantification are in the range of ppb. These limits are especially low for high molecular PAHs which are a potential risk for human health. Some of these compounds are considered as dangerous priority substances in the legislation so that method is suitable to make analysis in accordance with the concentrations of the directive 2008/105/CE [5]. This guarantees that the method is capable to detect and quantify concentrations below of the concentrations established in the legislation.

The directive established the maximum authorized concentrations for anthracene, fluoranthene, benzo(a)pyrene which are 0,4, 1 and 0,1 ppb respectively. For benzo(b)fluoranthene the sum of its concentration and the concentration of its isomer benzo(k)fluoranthene should not exceed 0,03 ppb per year. The values obtained for fluoranthene in the Puerto de Las Nieves (Agate) follow the legislation. However, the concentration of anthracene exceeds the concentration established in the legislation for all the places. The benzo(a)pyrene was not detected in any sample. The benzo(b)fluoranthene was detected only in the Muelle Deportivo and in the intake water of PLOCAN at

concentrations of 0,05 and 0,06 ppb. It cannot be determined if this compound follows the legislation due to there is only one data and it is necessary the data of a year to calculate the mean of concentrations for this purpose.

5. Conclusion

The developed method for extraction of contaminants from seawater has been validated and applied with success to the determination of PAH in coastal waters of Gran Canaria. This extraction system is miniaturized and portable and will be implemented in oceanographic buoy in the future.

The method has been optimized and validated through the determination of PAH by high performance liquid chromatography (HPLC). The method detected and quantified at concentrations below of the concentrations established in the legislation. This method was used for the quantification of PAHs in real samples around of Gran Canaria. With the developed and validated method, it is working in the isolation of the peristaltic pump for couple it into an oceanographic buoy SeaMon-HC of small size and installable in ports.

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Memoria del TFG

- Descripción detallada de las actividades desarrolladas durante la realización del TFG

Las actividades consistieron en búsqueda bibliográfica para completar el contenido del TFG. Se realizaron presentaciones en power point con lo que se había avanzado y se expusieron en Inglés para por un lado desenvolverme con el inglés y por otro lado para que la tutora académica evaluara que es lo que había hecho hasta la fecha y corregirme algunas cosas. A parte se realizó la redacción del TFG, búsqueda de figuras, realización de la presentación definitiva, traducción del TFG, etc.

- Formación recibida (cursos, programas informáticos, etc.)

No se recibió ningún tipo de formación adicional reglada, si se formó sobre el manejo del cromatógrafo líquido de alta resolución (HPLC) y del software de control para el procesamiento de los datos obtenidos.

- Nivel de integración e implicación dentro del departamento y relaciones con el personal.

La integración fue óptima en todo momento y la realización de labores se llevó a cabo en los tiempos estipulados. La relación con la tutora académica fue comunicativa así como su disposición fue total en todo momento.

- Aspectos positivos y negativos más significativos relacionados con el desarrollo del TFG

Como aspectos positivos cabe destacar el aprendizaje de habilidades como la escritura, la elaboración de un artículo, el procesamiento de datos, la mejora en el inglés redactado así como el contenido sobre el que versa el TFG.

Como aspecto negativo destaco quizás que a lo largo de la carrera podrían hacer algo más de hincapié en la redacción de este tipo de artículos y en el uso del inglés en distintos ámbitos.

- Valoración personal del aprendizaje conseguido a lo largo del TFG.

Considero la valoración final como satisfactoria por lo enriquecedor de la experiencia así como por las habilidades y el conocimiento adquirido. La motivación fue mucha y la satisfacción bastante buena en general.