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Evaluation of single-walled carbon nanohorns as sorbent in dispersive micro solid-phase extraction

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ABSTRACT

A new dispersive micro solid-phase extraction method which uses single-walled carbon nanohorns (SWNHs) as sorbent is proposed. The procedure combines the excellent sorbent properties of the nanoparticles with the efficiency of the dispersion of the material in the sample matrix. Under these conditions, the interaction with the analytes is maximized. The determination of polycyclic aromatic hydrocarbons was selected as model analytical problem. Two dispersion strategies were evaluated, being the functionalization via microwave irradiation better than the use of a surfactant. The extraction was accomplished by adding 1 mL of oxidized SWHNs (o-SWNHs) dispersion to 10 mL of water sample. After extraction, the mixture was passed through a disposable Nylon filter were the nanoparticles enriched with the PAHs were retained. The elution was carried out with 100 μL of hexane. The limits of detection achieved were between 30 and 60 ng L^{-1} with a precision (as repeatability) better than 12.5%. The recoveries obtained for the analytes in three different water samples were acceptable in all instances. The performance of o-SWNHs was favourably compared with that provided by carboxylated single-walled carbon nanotubes and thermally treated carbon nanocones.

1. Introduction

The recent years have witnessed the burst of the nanoscience and nanotechnology in almost all scientific areas. The reason behind such enormous impact is that, on the nanometer scale, the properties of matter can differ from those in the micro and macroworld and even depend not only on the chemical composition and phase but also on the size of the given materials. It envisages relevant advances in imaging, electronics and therapeutics. Nanomaterials are already present in chips, sporting goods, clothing, cosmetics and dietary supplements with numerous forthcoming applications such as pharmaceutical formulations. As nanomaterials are unique because of their nanometer scale, their exceptional properties are maintained as far as the nanometric dimensions prevail [1].

Analytical Chemistry has also taken benefit from the exceptional chemical, electric, optical, thermal or magnetic properties of nanoparticles to simplify and miniaturize the chemical measurement processes in general, and sample treatment in particular [2]. Among the different steps that can be included in the preliminary operations of the analytical process, separation techniques are ubiquitous as they permit the analytes isolation (improving selectivity) and preconcentration (increasing sensitivity) and also compatibility of the media with the instrumental technique used. The miniaturization of the separation techniques and more specifically the liquid and solid phase extraction approaches is a current trend in analytical chemistry as it improves the productively related analytical properties in terms of expeditiousness and cost [3,4]. The success of miniaturized extraction techniques relies on their efficiency and it is directly related to the properties of the extractant (liquid phase or sorbent material). In the context of the solid-phase microextraction, several approaches have been proposed in the literature in which the extraction is carried out in a fiber or a stir bar [5,6]. The wide use of these miniaturized approaches grounds on the commercially available devices which are in some cases fully compatible with the analytical instruments, such as the powerful combination between in-fiber SPME and gas chromatography. The sorbents used in the miniaturized approaches must present a high surface area in order to maximize the interaction with the analytes. This requirement is not present in conventional sorbents but it is an outstanding property of nanostructured materials. The high aggregation tendency of such nanoparticles, and most concretely carbon-based ones, clearly limits their applicability in this context because the properties are associated with the nanometric scale and they are diminished when the nanoparticles are aggregated [7].

Dispersive solid phase extraction was proposed in 2003 as a very efficient procedure to increase the selectivity of the analytical processes [8]. It was focused on the determination of pesticides

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in fruits and vegetables. In the general procedure, the solid is selected to interact with the interferents (pigments, sugars, or lipids) while the analytes remain in the liquid phase. This technique has been recently proposed to improve the sensitivity of the process by adding few amounts of sorbent (in the very low mg range) and once retained the analytes are eluted, thermally desorbed or directly monitored by spectroscopic techniques [9–11]. As far as nanoparticles is concerned, magnetic ones have been proposed in the literature taking into account that after extraction, they can be separated from the liquid media by means of a magnet, which simplifies the process as no centrifugation step is required. It has been used to determine PAHs [12] and UV-filters [13] in water samples.

In this paper, a novel dispersive micro solid-phase extraction (μ-SPE) using carbon nanohorns as active sorbent is presented. The dispersion of the nanoparticles has been deeply studied in order to maximize the efficiency of the extraction. Moreover, the whole procedure was optimized in order to achieve the highest recoveries. Polycyclic aromatic hydrocarbons were selected as model compounds taking into account their aromaticity, which clearly favours the interaction with the carbon nanohorns and also their consideration as priority pollutants. Finally, the performance of carbon nanotubes and carbon nanocones was also evaluated in order to compare their behaviour in the optimized dispersive micro solid-phase extraction conditions.

2. Experimental

2.1. Reagents and samples

All reagents were of analytical grade or better. Polycyclic aromatic hydrocarbons: acenaphthene, anthracene, benzo(a)anthracene, fluoranthene, fluorene, naphthalene, phenanthrene and pyrene were purchased from Sigma–Aldrich (Madrid, Spain). Stock standard solutions of individual analytes were prepared in methanol at a concentration of 1 g L^{-1} and stored at 4 °C. Working standard solutions were prepared on a daily basis by rigorous dilution of the stocks in ultrapure water or methanol (Sigma–Aldrich) as required.

Single-walled carbon nanohorns (SWNHs) were purchased from Carbonium S.r.l. (Padua, Italy). These nanoparticles were produced by direct graphite evaporation in Ar flow with purity above 90%. According to information reported by the manufacturer, SWNHs form dahlia-shaped stable aggregates with an average diameter of 60–80 nm. Individually, each nanohorn has a variable length between 40 and 50 nm and a diameter in the cylindrical nanostructure ranging between 4 and 5 nm.

Carbon nanocones/disks high grade, were supplied by n-Tec (Oslo, Norway). This solid material is composed of 20 wt% carbon nanocones, 70 wt% carbon disks and 10 wt% amorphous carbon black. The carbon nanocones are characterized by a length between 300 and 800 nm, and a maximum base diameter between 1 and 2 μm. Moreover, the thickness of the wall is in the range 20–50 nm.

Single-walled carbon nanotubes and single-walled carbon nanotubes functionalized with carboxyl groups (c-SWNTs) were also used. The raw SWNTs were purchased from Sigma–Aldrich (Madrid, Spain). They present an approximate purity of 90%, an external diameter of 1–2 nm and variable length of 0.5–2 μm. Functionalized SWNTs were supplied by Cheap Tubes Inc. (Brattleboro, USA) with a purity exceeding 95%. These c-SWNTs present an outer diameter on 20–30 nm and lengths from 10 to 30 nm approximately.

River, tap and bottled water were selected for the determination of the target PAHs following the proposed dispersive micro-solid phase extraction approach. Bottled water was purchased in local markets and they were packed in 500 mL plastic containers. They were maintained refrigerated in their original packing until analysis. Water samples for the Genil river were collected in amber glass bottles without headspace and stored at 4 °C until analysis. The sample pH was 6.9 and all the aliquots were filtered through a 0.45 μm disposable Nylon filter prior to analysis.

2.2. Apparatus

Functionalization of SWNHs was carried out using a household microwave oven equipped with a magnetron of 2450 MHz with a nominal maximum power of 800 W as marketed. For the complete dispersion of the oxidized SWNHs (o-SWNHs), a centrifuge and an ultrasonic bath, both from Selecta (Barcelona, Spain) were employed. A Vortex agitator (Heidolph, Mérida, Spain) was also used.

Chromatographic analyses were carried out on a gas chromatograph (Varian CP-3800)–mass spectrometer (Varian 1200 MS/MS) equipped with triple quadrupole analyzer and an electron multiplier detector. PAHs were separated on a fused silica capillary column VF-5 ms (30 m × 0.25 mm i.d.), coated with 5% phenyl – 95% dimethylpolysiloxane (film thickness 0.25 μm) (Supelco, Madrid, Spain). The temperature program of the chromatographic oven began at 60 °C (2 min), ramped to 240 °C at 35 °C min^{-1} and then to 300 °C at 15 °C min^{-1}. This final temperature was held for 5 min. The injection port was maintained at 250 °C throughout the experiments. A column split ratio of 1:10 was selected for the manual injection of 2 μL using a 5 μL microsyringe (Hamilton Co., Nevada, USA). Helium (6.0 grade, Air Liquide, Seville, Spain) at a flow rate of 1.4 mL min^{-1}, regulated by a digital pressure and flow controller, was used as the carrier gas. Electron impact ionization (EI) was used with an ionization energy of 70 eV. The transfer line and ionization source were maintained at 280 °C and 250 °C, respectively. Mass spectra were acquired using the selected ion monitoring mode, recording the following fragment-ions: 128 (from 5.1 to 6.4 min), 154 (from 6.4 to 6.8 min), 166 (from 6.8 to 7.5 min), 178 (from 7.5 to 8.5 min), 202 (from 8.5 to 10.2 min) and 228 (from 10.2 to 12.3 min) at 5 scan s^{-1}. Total ion current chromatograms were acquired and processes using MS Workstation (Varian) on a AMD Sempro™ Processor computer which also controlled the whole system.

2.3. Preparation of the dispersion of single-walled carbon nanohorns

The procedure was as follows. First, an amount of 10 mg of pure SWNHs was accurately weighted in a glass vial. Subsequently, the nanomaterial was subjected to a functionalization using microwave energy (800 W, 10 min) [14]. According to the authors, this process generated oxygenated functional groups on the nanoparticle surface, which could facilitate their dispersion in polar media. Then, the functionalized solid was dispersed in 50 mL of Milli-Q water and then stirred for 60 min in an ultrasonic bath. The dispersion was centrifuged at 10,000 rpm for 15 min to remove potential non-functionalized material, thus improving the reproducibility between dispersions. The dispersions obtained are stable for ca. 24 h being possible their re-suspension by the application of ultrasounds for 1 h. Experiments carried out using several o-SWNHs dispersions prepared in different days showed a high batch-to-batch reproducibility.

2.4. Dispersive micro solid-phase extraction procedure

The proposed miniaturized extraction method was as follows: An aliquot of 10 mL of sample or an aqueous standard containing the eight PAHs at concentrations within the linear range was placed in a 20 mL glass vial. Next, 1 mL of the dispersed o-SWNHs at a final concentration of 0.2 g L^{-1} was added. Subsequently, the vial

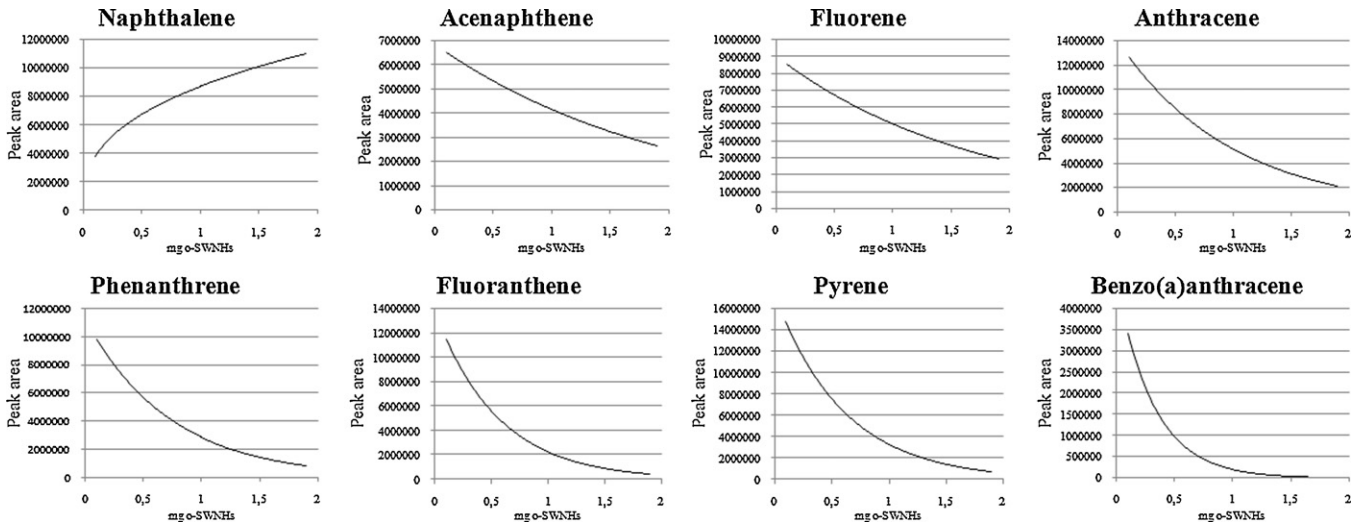

Fig. 1. Influence of the amount of o-SWNHs dispersed in the extractant on the chromatographic peak area of the selected PAHs.

was sealed and stirred at 1600 rpm for 2 min. Homogenization was immediately achieved, which promotes the interaction between the analytes and carbon nanoparticles. Once the extraction was completed, the whole volume was passed through a 0.45 μm disposable nylon filter (13 mm i.d.) previously conditioned passing 5 mL of hexane and 5 mL of Milli-Q water. The o-SWNHs enriched with the analytes were retained on the filter while the aqueous phase was discarded. Then the elution of the PAHs was accomplished by passing 100 μL of hexane through the filter. The eluate was collected in a vial and 2 μL injected in the gas chromatograph - mass spectrometer for further qualitative and quantitative analysis.

2.5. Safety considerations

The organic solvents and analytes used in this work are relatively volatile and slightly toxic and they should be handled using protective gloves and face mask. All the wastes were collected in special bottles for a proper management. The nanoparticles were handled under the above described safety considerations.

3. Results and discussion

3.1. Preliminary experiments

In previous research of our group, it was established the usefulness of single-walled carbon nanohorns as stationary phase in capillary electrochromatography [15]. However, no references have been published up to date dealing with the use of single-walled carbon nanohorns in solid phase extraction. Therefore, our first interest was to evaluate their sorbent capacity, using PAHs as model analytes taking into account their hydrophobic and aromatic characteristics. For this purpose, 10 mg of SWNHs were packed in a conventional SPE cartridge and 10 mL of an aqueous standard containing the PAHs at a concentration of 500 $\mu g\,L^{-1}$ were passed through the sorbent. The aqueous phase was collected in a glass vial, extracted with 1 mL of hexane and injected in the GC–MS for analysis. As a result, no signal for the target compounds was observed in the chromatogram at the corresponding retention times. The elution of the retained PAHs was accomplished by using 1 mL of hexane, the analytes being identified at their characteristics retention times although the signal was low. It was attributed to the technical problems in the packing of the sorbent as it was very difficult to maintain the nanoparticles in the low part of the cartridge as they tend to be deposited on the walls. However, the absence of the analytes in the aqueous phase corroborates the potential sorption capacity of the nanoparticles. In order to overcome the problems associated with the packing of the SWNHs and to reduce the aggregation of the nanoparticles, which results in a lower sorption capacity, the dispersion of the SWNHs in water was accomplished in order to use the final dispersed nanoparticles as extractants of the PAHs.

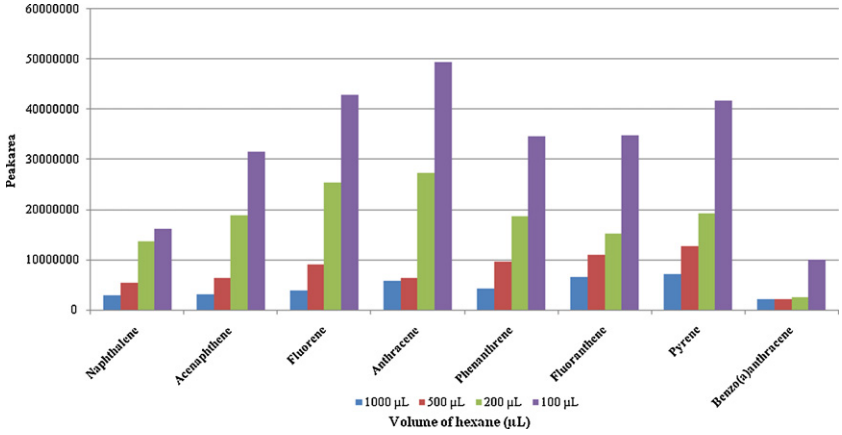

Fig. 2. Effect of the volume of hexane on the chromatographic peak area of the selected PAHs.

Table 1
Analytical figures of merit of the proposed dispersive micro solid-phase extraction method using o-SWNHs as sorbent material.

Analyte	*m/z*	Limit of detection ($ng\,L^{-1}$)	Limit of quantification ($ng\,L^{-1}$)	Relative standard deviation (%, n = 5)	Absolute extraction recovery (%)
Naphthalene	128	50	150	11.9	96
Acenaphthene	154	40	120	5.3	69
Fluorene	166	30	100	8.1	83
Anthracene	178	30	100	7.7	80
Phenanthrene	178	40	120	10.9	89
Fluoranthene	202	40	120	7.1	86
Pyrene	202	40	120	12.5	37
Benzo(a)anthracene	228	60	200	7.2	21

3.2. Initial conditions for the dispersive micro solid-phase extraction

The dispersion of the carbon nanohorns in an aqueous medium can be achieved by following two main approaches: (a) the addition of a surfactant to the raw material; or (b) the functionalization via oxidation to increase the solubility in the aqueous phase. Both alternatives were evaluated.

Surfactant coated single-walled carbon nanohorns were prepared by adding 25 mg of the nanoparticles to 25 mL of a 17 mM sodium dodecyl sulphate (SDS) aqueous solution. Then, the mixture was sonicated for 60 min. Functionalizated single-walled carbon nanohorns were obtained by microwave irradiation of the raw solid (25 mg) for 10 min at 800 W. Then, the oxidated nanoparticles were dispersed in 25 mL of water using ultrasounds radiation for 60 min. Both dispersions were evaluated for the extraction of PAHs from waters, being acenaphthene selected as model analyte.

For this purpose, 5 mL of a standard solution of acenaphthene, prepared at a concentration of $500\,\mu g\,L^{-1}$, were placed in a vial and 1 mL of the dispersed SWNHs (surfactant coated or oxidized) was added. The mixture was mixed using a vortex for 2 min. Then, the dispersion was passed through a 0.45 μm Nylon filter where the nanoparticles enriched with the analytes were retained while the aqueous phase was discarded. The elution was accomplished by passing 1 mL of hexane through the filter and aliquots of 2 μL of the organic extract were injected into the GC–MS for analysis. In order to determine the potential contribution of the SDS micelles in the extraction, and extraction of the acenaphthene aqueous standard using 1 mL of 17 mM SDS solution was also carried out. From this experiment, it was concluded that the highest recovery (ca. 35% better) was achieved when the oxidized SWNHs were used. Moreover, it was also observed that the extraction with SDS and surfactant coated SWHNs was very similar. It can be attributed to the fact that the reduced dimensions of the SWNHs included in the core of the SDS micelles, did not present a synergic contribution to the extraction process. Therefore, o-SWNHs were used as dispersed phase for subsequent experiments.

3.3. Selection of the o-SWNHs dispersive micro solid-phase extraction conditions

The initial values for the different variables involved in the extraction process were fixed as follows: Sample, 2.5 mL of an aqueous standard containing the PAHs at a concentration of $50\,\mu g\,L^{-1}$; extractant: 2.5 mL of o-SWNHs ($1\,g\,L^{-1}$) dispersed in water; vortex agitation for 5 min and filtration of the aqueous phase through a 0.45 μm disposable Nylon filter (25 mm internal diameter); eluent: methanol, 500 μL.

The first variable studied was the eluent. For this purpose, organic solvents compatible with the instrumental technique (GC–MS) were evaluated, namely: methanol, hexane, acetone and acetonitrile. In all cases, the volume was fixed at 500 μL. Hexane provided the best results in terms of chromatographic peak areas. Moreover, the chromatograms were cleaner in comparison with those obtained with the other solvents and therefore, it was chosen for further studies.

The concentration of o-SWHNs in the aqueous dispersion (extractant) affects to the sensitivity of the determination with two opposite effects. On the one hand, higher concentration of nanoparticles will lead to higher enrichment factors. On the other hand, it also increases the aggregation of the o-SWNHs which effectively reduces the nanoparticles surface available to interact with the analytes. This variable was studied in the interval 1–0.1 $g\,L^{-1}$. The best results were obtained when a concentration of $0.2\,g\,L^{-1}$ was used, which corroborates the negative influence of the aggregation in the extraction capacity of the carbon nanoparticles, in general, and o-SWNHs in particular.

Table 2
Recovery study of the selected PAHs from three different water samples using the proposed dispersive micro solid-phase extraction method.

Analyte	Concentration added ($\mu g\,L^{-1}$)	Tap water	River water	Bottled mineral water
		(%, n = 3)	(%, n = 3)	(%, n = 3)
Naphthalene	5	57 ± 6	59 ± 6	60 ± 6
	100	96 ± 12	97 ± 12	96 ± 11
Acenaphthene	5	47 ± 2	56 ± 2	72 ± 5
	100	68 ± 4	110 ± 6	103 ± 5
Fluorene	5	52 ± 4	71 ± 6	61 ± 5
	100	93 ± 8	100 ± 8	83 ± 7
Anthracene	5	52 ± 4	92 ± 8	64 ± 4
	100	88 ± 7	94 ± 8	99 ± 8
Phenanthrene	5	25 ± 2	93 ± 10	57 ± 5
	100	78 ± 8	84 ± 9	101 ± 11
Fluoranthene	5	66 ± 5	73 ± 5	69 ± 5
	100	90 ± 7	74 ± 5	92 ± 7
Pyrene	5	60 ± 7	92 ± 11	69 ± 8
	100	88 ± 10	78 ± 9	85 ± 10
Benzo(a)anthracene	5	90 ± 6	88 ± 7	50 ± 4
	100	80 ± 6	61 ± 4	88 ± 7

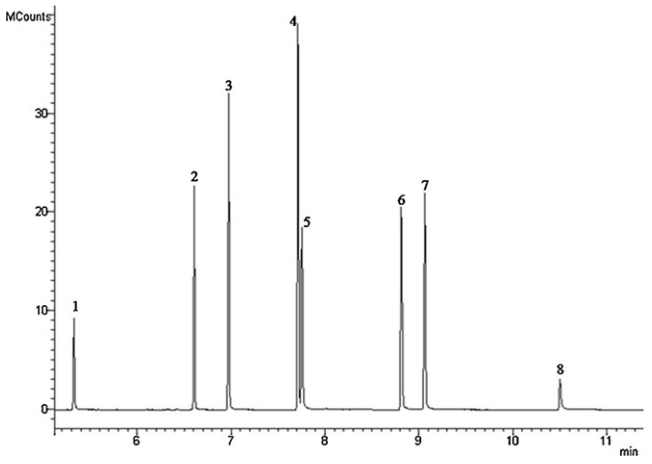

Fig. 3. Selected ion monitoring gas chromatogram obtained for a tap water sample spiked with the PAHs at a concentration of 100 μg L^{-1}. Peaks: 1, Naphthalene; 2, Acenaphthene; 3, Fluorene; 4, Anthracene; 5, Phenanthrene; 6, Fluoranthene; 7, Pyrene; 8, Benzo(a)anthracene.

Next, the extractant to sample ratio was evaluated. For this study, a final volume of 10 mL and a concentration of 50 μg L^{-1} for all the analytes were fixed in all the experiments. The results obtained are depicted in Fig. 1, where the variations of the peak areas versus the volume of dispersed o-SWNHs are represented. As it can be seen, for all of the PAHs, there was a decrease in the peak area when the volume of dispersed extractant increases, except for naphthalene, whose signal remained almost constant within interval. Therefore, a 1:9 extractant:sample volumes ratio was selected as optimal.

The eluent volume influences the sensitivity of the method as it determines the maximum preconcentration factor that can be achieved for the target analytes. Ideally, it should be as low as possible but providing a quantitative and reproducible elution of the compounds. The hexane volume was studied between 100 and 1000 μL, the results being summarized in Fig. 2. For values higher than 500 μL, 25 mm i.d. filters were used while smaller ones (13 mm i.d.) were used for lower volumes. The equivalence of these filters was corroborated as the same signal was obtained for 500 μL in both cases. As it can be seen, the best results were obtained for 100 μL due to the highest analytes preconcentration. Moreover, the elution was quantitative as when a fresh volume of hexane was passed through the filter, no analytical signal was obtained. Therefore, 100 μL of hexane was selected as optimum.

The last variable studied was the extraction time in the vortex. It was evaluated in the interval 30 s to 10 min. The peak areas for all PAHs increased with the extraction time up to 2 min, remaining almost constant over this value, being thus selected as optimum.

3.4. Analytical figures of merit of the SWNHs dispersive micro solid-phase extraction

The optimized miniaturized dispersive extraction method was characterized in terms of sensitivity, linearity and precision. The calibration graphs were constructed for the eight PAHs selected using aqueous standards extracted under the optimized conditions. The limits of detection were calculated as the minimum concentration providing a chromatographic peak area three times higher than the background noise. The values are listed in Table 1 and they varied between 30 and 60 ng L^{-1}. The linearity was between 100 ng L^{-1} and 500 μg L^{-1}. The precision of the method (expressed as relative standard deviation) was calculated for eight individual standards prepared at 500 ng L^{-1} ranged between 5.3% (acenaphthene) and 12.5% (pyrene).

Also, the absolute extraction recoveries were evaluated for each PAH. This parameter is defined as the percentage of total analyte that can be efficiently extracted by the o-SWNHs and further eluted with hexane. They are presented in Table 1 and ranged from 21 to 96%, the lower values being obtained for the heavier PAHs. The absolute extraction recoveries obtained demonstrated the efficiency of the dispersed nanoparticles for the extraction of the PAHs as these values are higher that those provided by other micro solid phase extraction techniques which do not use the dispersion of the sorbent material.

Recovery studies were carried out by spiking the selected PAHs to tap, river and bottled mineral water samples at two concentration levels, 5 and 100 μg L^{-1}. In order to evaluate the applicability of the proposed method to the analysis of water samples, a recovery study was carried out in tap, river and bottled water. The samples were analyzed after collection and no signal for the target analytes were obtained. Then, the samples were spiked with the selected PAHs at two concentration levels, 5 and 100 μg L^{-1} and left stand for 76 h after enrichment in order to allow potential interactions between the PAHs and the sample matrix. The results obtained are listed in Table 2. The average recoveries for each matrix were 74% (tap water), 83% (river water) and 78% (bottled mineral water). By way of example, Fig. 3 shows the chromatogram obtained for a tap water sample spiked with the target PAHs at a concentration of 100 μg L^{-1}.

3.5. Comparison with carbon nanotubes and carbon nanocones

As it was stated in previous section of this article, the potential of carbon nanoparticles in solid-phase extraction is well-established

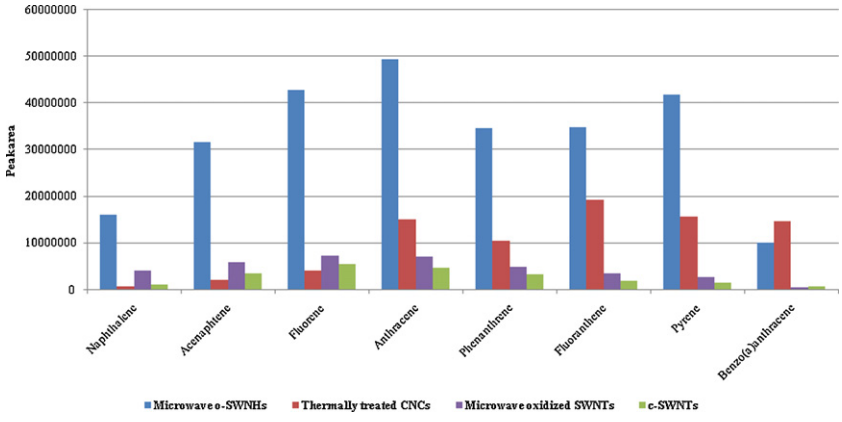

Fig. 4. Comparison of the performance of single-walled carbon nanohorns, single-walled carbon nanotubes and carbon nanocones in dispersive micro solid-phase extraction.

[7,16]. Therefore, the efficiency of o-SWNHs in dispersive μ-SPE was compared with that provided by single-walled carbon nanotubes and carbon nanocones.

For this purpose, thermally treated carbon nanocones [17], single-walled carbon nanotubes functionalized by microwave radiation and carboxylated single-walled carbon nanotubes were dispersed under the optimized conditions of the method. Stable dispersions were obtained for the thermally treated carbon nanocones and the carboxylated single-walled carbon nanotubes, while the carbon nanotubes treated with microwave radiation presented a certain degree of aggregation. In all cases, the concentration of the carbon nanoparticles was 0.2 g L^{-1} and the optimized experimental conditions were used in this comparison. The results are illustrated in Fig. 4. As a general conclusion, it can be said that the best extraction was achieved with the conical nanoparticles as the sorption on the carbon nanotubes was, in comparison, very low. In general, o-SWNHs were the best sorbent in dispersive μ-SPE for all the PAHs, being only slightly better carbon nanocones for the solation of benzo(a)anthracene. However, it should be noted that the efficiency of the dispersive μ-SPE using carbon nanocones increased when increasing the number of aromatic rings in the PAH. This behaviour can be explained taken into consideration the dimensions of carbon nanocones, which are ca. 20 times larger than the SWNHs. The lower size of the o-SWNHs favours the interaction on the nanoparticle surface. In addition, the base diameter of carbon nanocones varied between 1 and 2 μm. This will allow the interactions of the PAHs in the inner part of the nanoparticle, being more difficult their release in the elution step. It also causes a poor reproducibility in the extractions.

4. Conclusions

The research presented in this article demonstrated the potential of o-SWNHs as sorbent in miniaturized solid phase extraction techniques. The dispersive approach focused on sensitivity enhancement overcomes the main limitation of the use of carbon nanoparticles in solid phase extraction techniques as it is their aggregation. Different methodologies for the dispersion were evaluated, being the functionalization with microwave energy the most suitable for this aim. The dispersed nanoparticles are stable more than 24 h and the reproducibility of the extraction acceptable for the analytical problem studied. Moreover, the comparison with typical carbon nanoparticles such as carbon nanotubes and carbon nanocones, which are more similar in shape and electronic distribution, pointed out the better performance of conical carbon nanoparticles in dispersive μ-SPE. The differences in size between carbon nanohorns and carbon nanocones also conditions their affinity for a specific group of PAHs, which are also retain in a different way on the two carbon nanoparticles. The carbon nanocones are by far the cheapest among the carbon nanoparticles (ca 33 $/g) although its purity is the lowest (20% cones and 70% disks). However, they can be easily purified by thermal treatment. The carbon nanohorns are cheaper (ca. 200 $/g) than the single walled carbon nanotubes (ca. 950 $/g) and of higher purity. In addition, it is also inexpensive their functionalization and almost all the solid is functionalized while the carboxylated nanotubes are very expensive (ca. 2300 $/g); also the laboratory functionalization is rather tedious and with a low percentage of functionalization. In our opinion, the SWNHs are the best alternative among carbon nanoparticles in terms of efficiency and cost. Concerning other conventional solid sorbents, the highest retention capacity of o-SWNHs, which allows the reduction of the dimensions of the extraction procedure, can be highlighted as the capital advantage. It also reduces the eluent (organic solvent) volume required, which makes the cost and environmental aspects of the method more favourable.

Further studies will be aimed at evaluating the behaviour of carbon nanohorns in dispersive μ-SPE for the isolation of different families of compounds of variable polarity.

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