

Single-walled carbon nanohorns immobilized on a microporous hollow polypropylene fiber as a sorbent for the extraction of volatile organic compounds from water samples

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Received: 30 October 2013 / Accepted: 14 February 2014 / Published online: 12 March 2014
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Abstract We have evaluated the behavior of single-walled carbon nanohorns as a sorbent for headspace and direct immersion (micro)solid phase extraction using volatile organic compounds (VOCs) as model analytes. The conical carbon nanohorns were first oxidized in order to increase their solubility in water and organic solvents. A microporous hollow polypropylene fiber served as a mechanical support that provides a high surface area for nanoparticle retention. The extraction unit was directly placed in the liquid sample or the headspace of an aqueous standard or a water sample to extract and preconcentrate the VOCs. The variables affecting extraction have been optimized. The VOCs were then identified and quantified by GC/MS. We conclude that direct immersion of the fiber is the most adequate method for the extraction of VOCs from both liquid samples and headspace. Detection limits range from 3.5 to 4.3 ng L⁻¹ (excepted for toluene with 25 ng L⁻¹), and the precision (expressed as relative standard deviation) is between 3.9 and 9.6 %. The method was applied to the determination of toluene, ethylbenzene, various xylene isomers and styrene in bottled, river and tap waters, and the respective average recoveries of spiked samples are 95.6, 98.2 and 86.0 %.

Keywords Oxidized single-walled carbon nanohorns · (Micro)solid phase extraction · Waters · Volatiles compounds · Nanotechnology

Introduction

Volatile pollutants are an environmental problem because they are widely distributed on account of their easy transport through the media. The origin of these compounds can be either natural or anthropogenic. Contamination of surface and ground waters with volatile aromatic compounds is one of the main environmental problems today. Benzene, toluene, ethylbenzene, xylene isomers and styrene (BTEX-S) constitute the most representative family of the volatile aromatic compounds. They are routinely used in the industry as raw materials and as solvents and they can be present in many oil derivatives. These types of aromatic compounds are widespread pollutants and they are ubiquitous in the different environmental compartments. BTEX-S are highly toxic and they have low biodegradability. Indeed, they can easily penetrate in humans through ingestion, inhalation or absorption, producing different effects for health and comprising a high toxicity [1]. The effects negatives depend on the nature of each compound and the degree and period of exposure.

The analytical methods designed for the analysis of environmental samples for the determination of BTEX-S must reach the legal limits fixed for these compounds. Taking into account the low values established, the direct analysis of the samples is unfeasible, being necessary the inclusion of a preconcentration step [2, 3].

Solid phase microextraction (SPME) was first proposed in 1990 by Arthur and Pawliszyn [4]. It can be considered as a miniaturized sample pretreatment technique

Electronic supplementary material The online version of this article (doi:10.1007/s00604-014-1211-z) contains supplementary material, which is available to authorized users.

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whose advantages over other well-established methods have been clearly identified. The type of coating used in SPME plays a crucial role in the efficiency of the extraction as it is the main factor affecting the distribution constant between the target compounds and the immobilized phase [5]. In this context, the synthesis and development of new materials with enhanced sorption capacity can be considered a milestone in the evolution of this technique. Among them, nanostructured solids have emerged as useful tools for solid phase microextraction. Carbon nanostructures [6], silica [7] and titanium dioxide [8], as well as hybrid nanoparticles [9, 10] have been reported in the literature as new coating in miniaturized solid phase extraction devices.

Single-walled carbon nanohorns (SWNHs) have horn-shaped tips, diameter of 2–5 nm, tubule length of 40–50 nm and cone angle of approximately 20°. They can be produced in big amounts with high purity [11, 12]. The individual SWNHs present an extensive surface area and also their aggregates and the inner and external interstices provide them with an enhanced adsorption capacity as regards other carbon nanostructures. Moreover, the surface area can be increased by opening sidewall nanowindows [13–17] which permits the inclusion of small molecules (e.g. fullerenes or iron nanoparticles). The oxidation conditions influence the size of the nanowindows, allowing the preparation of different molecular sieves by controlling the operational variables [16, 17]. The sorbent capacity of single-walled conical nanoparticles was first demonstrated by their storage capacity of hydrogen and deuterium [18]. This property can also be exploited not only for material storage and further progressive delivery [19–21], but also for the isolation and preconcentration of analytes in miniaturized extraction techniques [22, 23].

This study evaluates the potential of the carbon nanohorns as sorbent material immobilized in the pores of a hollow fiber for preconcentration of toluene, ethylbenzene, xylene isomers and styrene from waters. The sorbent capacity of this extraction unit has been previously demonstrated by our research group using triazines as model analytes [23]. Taking into account, the lower volatility of the herbicides, the extraction was carried out under the direct immersion configuration. The selection of more volatile aromatic compounds permits the performance comparison of the miniaturized extraction unit under the direct immersion and headspace to explore the potential of the extraction tool. For this purpose, all the variables affecting to the extraction process were deeply studied and the most favourable values were fixed. Under these conditions, both microextraction methods were characterized in terms of sensitivity, precision, linearity and accuracy, using fortified water samples in order to select the best alternative for the given analytical problem.

Experimental

Reagents and samples

All reagents were of analytical grade or better. Toluene, ethylbenzene, o-, m- and p-xylene (individual, pure compounds) and styrene (all of them named as TEXS), and deuterated o-xylene (internal standard) were purchased from Sigma-Aldrich (Madrid, Spain. <http://www.sigmaaldrich.com>). Stock standard solutions of individual analytes were prepared in acetone 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 Milli-Q water.

Single-walled carbon nanohorns were purchased from Carbonium S.r.l. (Padua, Italy. <http://www.carbonium.it/public/site/index.php>). The production of SWNHs was carried out, according to the information reported by the manufacturer, by direct graphite evaporation in Ar flow, and the purity obtained was above 90 wt%. SWNHs form stable dahlia-shaped aggregates with an average diameter of 60–80 nm. Individually, the lengths of these SWNHs are in a range 40–50 nm, and the diameter in the cylindrical structure varies between 4–5 nm.

Methanol (Sigma-Aldrich, HPLC gradient grade) was used for the dispersion of the oxidized single-walled carbon nanohorns (o-SWNHs) on the fiber pores, and n-hexane was used for TEX-S elution. Acetone was used for the preparation of the stock standard solutions of individual analytes.

The Q3/2 Accurel polypropylene microporous hollow fiber membrane (200 µm wall thickness, 600 µm inner diameter, 0.2 µm pore size, 75 % porosity) was obtained from Membrana (Wuppertal, Germany).

Tap, bottled and river water samples were selected for the determination of the target compounds using o-SWNHs hollow fiber (micro)solid phase extraction (o-SWNHs-HF-µSPE) approach. Water samples from the Guadalquivir River were collected in amber glass bottles without headspace and stored at 4 °C until analysis. All the aliquots were filtered using a 0.45 µm disposable Nylon filter prior to analysis. Bottled mineral water (1,500 mL, polyethylene terephthalate container) was purchased in local markets. All individual bottles were maintained refrigerated in their original packing until analysis.

Apparatus

Chromatographic analyses were carried out on a gas chromatograph (Varian CP-3800) – mass spectrometer (Varian 1200 MS/MS) working under single quadrupole mode and with an electron multiplier detector. The gas chromatograph was equipped with a fused silica capillary column VF-5 ms, (30 m x 0.25 mm i.d.) coated with 5 % phenyl – 95 %

dimethylpolysiloxane (film thickness 0.25 μm) (Supelco, Madrid, Spain) to separate the six analytes. The GC oven was programmed as follows: the initial temperature, 40 $^{\circ}\text{C}$, was maintained for 3 min and then raised to 60 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$. The final temperature, 280 $^{\circ}\text{C}$, was reached with a ramp of 40 $^{\circ}\text{C min}^{-1}$ and maintained for 2 min. The injector temperature was 225 $^{\circ}\text{C}$ and it was used in splitless mode. The injection volume of n-hexane, 2 μL , was measured with a 5 μL microsyringe (Hamilton Co., Nevada, USA). The carrier gas used was helium (6.0 grade, Air Liquide, Seville, Spain) at a flow rate of 1.0 mL min^{-1} , and it was regulated by a digital pressure and flow controller. The transfer line and ionization source were maintained at 280 $^{\circ}\text{C}$ and 250 $^{\circ}\text{C}$, respectively.

The ionization mode employed in the mass spectrometer was electron impact (EI) with ionization energy of 70 eV. Mass spectra were acquired using the selected ion monitoring mode (SIM), dividing the analysis time in two temporal windows, the first one with m/z 91 (from 4.80 to 7.93 min), and the second one selecting the m/z 91, 98 and 104 (from 7.93 to 9.0 min), all of them at 1 scan s^{-1} . Chromatograms were acquired and processed using MS Workstation (Varian) on an AMD SemproTM Processor computer which also controlled the whole system.

A JEOL JSM 6300 scanning electron microscopy (Isaza, Alcobendas, Spain) was also used to obtain the micrographs of the hollow fiber before and after the immobilization of the o-SWNHs.

A domestic microwave oven equipped with a magnetron of 2.450 MHz and a nominal maximum power of 800 W was used for SWNHs oxidation. An ultrasonic bath model 3510 from Branson (Connecticut, USA) was also used in different steps of the procedure. In the preparation of the fiber, an oven (Binder, Madrid, Spain) was used for drying the o-SWNHs hollow fiber at 80 $^{\circ}\text{C}$.

Preparation of the immobilized o-SWNHs hollow fiber

The miniaturized extraction unit was prepared following a procedure previously optimized by our research group [23]. Figure 1a shows the scheme of immobilization process o-SWNHs in porous hollow fiber. In brief, 5 mg of SWNHs were weighed and added to a glass vial, which was further introduced into a microwave oven, being the solid irradiated at 800 W for 10 min. This step generates oxygenated functional groups on the nanohorns surface. After cooling at room temperature, the oxidized carbon nanohorns were dispersed in 10 mL of methanol and sonicated for 30 min. The microporous hollow fiber, previously cut to a length of 2.5 cm, was introduced into the dispersion of o-SWNHs and sonicated for 30 min. Finally, the fiber was dried at 80 $^{\circ}\text{C}$ for 8 h in an oven.

Extraction unit device

The design of the extraction unit was aimed at obtaining the maximum efficiency of the extraction while maintaining good handling. For this purpose, a stainless steel wire was inserted into the hollow fiber in such a way that only the external surface of the fiber with the sorbent immobilized on the pores was available for the extraction of the analytes. In the final assembly, the stainless steel wire o-SWNHs hollow fiber was supported on a plastic film that can be placed on the top of the sample vial in order to fix the vertical position of the extraction unit during the extraction process (direct immersion or headspace configurations).

o-SWNHs hollow fiber (micro)solid phase extraction procedure

The analytical method developed for the extraction of the six target analytes from water samples using o-SWNHs hollow fiber μSPE is schematically depicted in Fig. 1b and it consists of the following steps.

Aliquots of 20 mL of aqueous standards or water samples containing the six target analytes were added to a 25 mL glass vial (DI) or 50 mL glass beaker (HS) containing a magnetic stirrer and 2 g (DI) or 4 g (HS) of NaCl. Then, the o-SWNHs-HF supported by a stainless steel wire was stucked to a plastic film and further placed on the top of the vial or beaker. Then, the fiber was vertically immersed in the liquid phase (DI) or maintained in the gaseous phase of the vial (HS), while the standard/sample was magnetically stirred for 15 min at 275 rpm (DI) or 410 rpm (HS). After this step, the analytes were eluted by immersing the hollow fiber in a glass insert containing 200 μL of n-hexane and sonicating in an ultrasonic bath for 5 min. Finally, 2 μL of the organic phase with the extracted analytes were injected into the gas chromatograph/mass spectrometer for their separation and detection. The chromatographic peak areas were used as analytical signals.

Between samples, the fiber was sequentially conditioned with 1.5 mL of n-hexane, acetone and Milli-Q water under sonication for 5 min in each case. Then, o-SWNHs-HF was dried in an oven at 80 $^{\circ}\text{C}$.

Following this procedure, the fiber can be reused for 20 times without a significant decreasing in the extraction efficiency.

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.

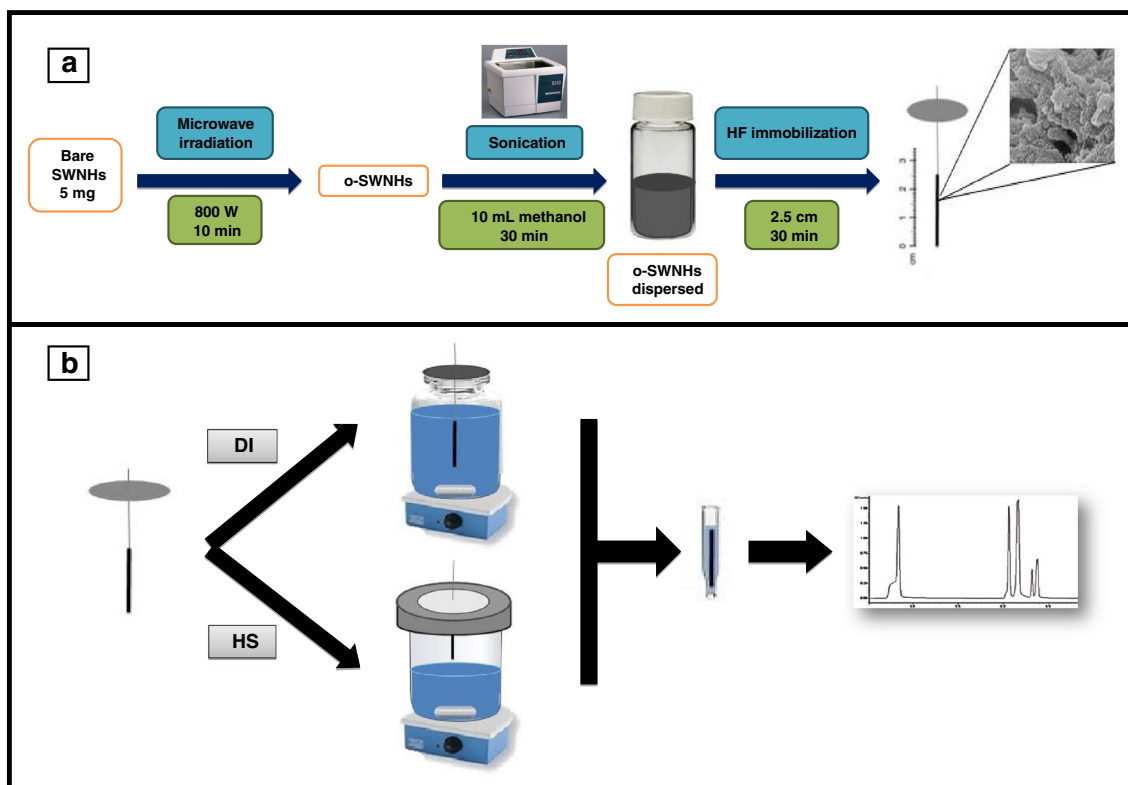


Fig. 1 **a** Scheme of immobilization process o-SWNHs in porous hollow fiber. **b** Schematic representation of the o-SWNHs hollow fiber μ SPE for the direct immersion (DI) and headspace (HS) extraction of volatile organic compounds from water samples

Results and discussion

Optimization of variables

The variables included in the optimization process were those related with the extraction/elution steps of both approaches, viz. direct immersion and headspace. In both cases, a univariate model was used in order to identify those variables that have a major influence on the process. The study was carried out using aqueous standard solutions containing the six volatile analytes (toluene, ethylbenzene, xylene isomers and styrene) at a concentration of 100 ng mL^{-1} . The initial experimental conditions for both methods were: 50 mL of aqueous standard without NaCl and magnetically stirred during 15 min at 410 rpm for the extraction, and elution with $200 \mu\text{L}$ of n-hexane assisted by sonication (15 min).

Optimization of the variables affecting to the direct immersion o-SWNHs hollow fiber μ SPE approach

The first variable optimized was the extraction time. As it can be seen in Fig. S1a (Electronic Supplementary Material, ESM), the chromatographic peak areas increased when increasing the extraction time up to 15 min. Therefore it was selected as the optimum extraction time in order to ensure the maximum efficiency of the process.

The next variable evaluated was the sample volume. Its influence was studied between 10 and 100 mL. The maximum signal was obtained for a volume of 20 mL. It was selected as optimum.

The salting-out effect was studied by adding solid NaCl to obtain a final concentration between 0 and 375 g L^{-1} . It was observed that the higher analytical signals for all analytes were obtained when 100 g L^{-1} of NaCl was added.

This salt concentration was used to evaluate the influence of the stirring rate of the sample in the analyte extraction was evaluated within the interval 0–825 rpm. As it is shown in Fig. S1b (ESM), the peak areas increased up to 225 rpm, decreasing over this value. It can be explained because a vortex was formed at higher rates and the fiber was not completely immersed into the liquid phase, thus reducing the efficiency of the extraction. Also, taking into account the volatility of the compounds, higher stirring rates would favour their release from the sample to the headspace of the vial.

The last variable optimized was the elution time. The elution step was carried out by the immersion of the o-SWNHs hollow fiber containing the target analytes into a glass insert with $200 \mu\text{L}$ of n-hexane, and different intervals, between 1 and 10 min, were tested. Five minutes were necessary to quantitatively elute the target analytes and it was fixed as optimum.

Optimization of the variables affecting to the headspace o-SWNHs hollow fiber μ SPE approach

The influence of the presence of an electrolyte (NaCl) in the sample on the efficiency of the extraction was studied between 0 and 375 g L⁻¹. The release of the analyte from to liquid phase to the headspace was favoured with increasing NaCl concentration up to 200 g L⁻¹, decreasing over this value. It can be ascribed to the higher viscosity of the liquid phase, This salt amount was selected for further experiments.

The agitation of the sample during the extraction was evaluated from 0 to 550 rpm. As it can be seen in Fig. S2a (ESM), the higher analytical signals for all target analytes were obtained with a stirring rate of 410 rpm. This fact corroborates the result obtained in the direct immersion approach, for which the optimum stirring rate was lower to reduce the release of the analyte to the headspace.

Concerning the extraction time, 15 min were enough to complete the process. The next variable studied was the extraction temperature. The analytical signal was evaluated in the range from 20 to 80 °C (Fig. S2b; ESM). As expected, the extraction decrease when increasing the temperature, due to the exothermic nature of the adsorption process on the fiber. Finally, another important variable for the extraction of the target analytes is sample volume. It was optimized in the interval 10–100 mL. A volume of 20 mL of sample was found to be adequate.

Analytical features of merit of o-SWNHs hollow fiber (micro)solid phase extraction methods

Once optimized, both approaches were characterized in terms of detection and quantitation limits, linearity, and precision. The main analytical features obtained for direct immersion and headspace microextraction are given in the following subsections.

Direct immersion

The corresponding calibration graphs were constructed by using aqueous standards containing the six analytes at

concentrations in the range 0.01–500 ng mL⁻¹ and the internal standard at 100 ng mL⁻¹. Standards were processed in duplicate using the optimized method, and 2 μ L of the organic extract was injected into the GC/MS for analysis. The corresponding equations were obtained by plotting the peak areas of the characteristic m/z fragment ions divided by that of the internal standard against the concentration for each target analyte. As it can be seen in Table 1, good linear relationship was obtained for all the analytes ($R > 0.9924$, toluene excepted).

The detection limits were calculated as the concentration providing an analytical signal three times higher than the background noise. They were in the range 3.5–4.3 ng L⁻¹ (25 ng L⁻¹ for toluene). The quantification limits were calculated as the concentration providing a chromatographic peak area ten times higher than the background noise and varied between 10.7 and 13.0 ng L⁻¹ for all analytes (80 ng L⁻¹ for toluene).

The precision of the method, expressed as relative standard deviation (RSD) was calculated from five individual standards prepared at a concentration of 50 ng mL⁻¹ and it was lower than 9.6 % for all the analytes. The enrichment factors for all the analytes were calculated by comparison of the slopes of the calibration graphs before and after the extraction process. They were in the range from 12.33 (for toluene) to 34.13 (for styrene).

Headspace

Calibration graphs were constructed similarly to the previously described procedure but in this case, the concentration range was 0.5 to 500 ng mL⁻¹ and the internal standard fixed at 100 ng mL⁻¹. The standards were processed following the optimized procedure, and 2 μ L of the organic extract was injected into the GC/MS for analysis. As it was the case with direct immersion modality, relative peak areas were plotted versus analyte concentration to calculate the linearity of the method for each compound. The results are listed in Table 2.

For all the analytes, a good linearity ($R > 0.9966$, toluene excepted) was observed. The detection limits

Table 1 Analytical figures of merit of the direct immersion o-SWNHs hollow fiber μ SPE for the determination of the target volatile organic compounds

Analyte	t_R (min)	m/z	R	LOD (ngL ⁻¹)	LOQ (ngL ⁻¹)	RSD (%; n=5)	EF
Toluene	4.83	91	0.9924	25.0	80.0	9.6	12.33
Ethylbenzene	6.05	91	0.9997	4.0	12.0	6.2	32.33
m- and p- xylene	6.15	91	0.9995	3.5	10.7	4.5	21.22
o- xylene	6.36	91	0.9996	4.3	13.0	3.9	26.50
Styrene	6.35	104	0.9994	3.9	11.8	4.3	34.13

t_R retention time, r correlation coefficient, LOD limit of detection, LOQ limit of quantitation, RSD relative standard deviation, EF enrichment factor

Table 2 Analytical figures of merit of the headspace o-SWNHs hollow fiber μ SPE for the determination of the target volatile organic compounds.

Analyte	t_R (min)	m/z	R	LOD (ngL ⁻¹)	LOQ (ngL ⁻¹)	RSD (%; n=5)
Toluene	4.83	91	0.9966	170	522	9.8
Ethylbenzene	6.05	91	0.9996	135	445	10.6
m- and p- xylene	6.15	91	0.9992	120	396	10.4
o- xylene	6.36	91	0.9999	138	455	13.3
Styrene	6.35	104	0.9991	127	419	8.7

t_R retention time, r correlation coefficient, LOD limit of detection, LOQ limit of quantitation, RSD relative standard deviation

were calculated as the concentration providing an analytical signal three times higher than the background noise. They were in the range 120–170 ng L⁻¹ and the quantification limits, calculated as the concentration providing a peak area 10 times higher than the background noise varied between 396 and 522 ng L⁻¹. The reproducibility of the method was evaluated at the limit of quantification in quintuplicate with results (expressed a relative standard deviation) in the range from 8.7 % (for styrene) to 13.3 % (for o- xylene).

The enrichment factors for all the analytes, which were obtained by comparing the slopes of the calibration graphs before and after the extraction process, were lower than 1 for all the analytes which is indicative of the low efficiency of the method for the analytical purpose, being the direct immersion approach more adequate to determine the target compounds in water samples.

Analysis of water samples

Finally, the accuracy of the o-SWNHs hollow fiber μ SPE was calculated. This analytical property can be calculated using either certified reference materials (CRMs) or quality control (QC) samples. As no CRM were available for this specific analytical problem, validation samples were prepared using

blank waters samples (river, tap, and mineral bottled waters) fortified with the six target analytes (toluene, ethylbenzene, (m+p)- and o-xylene, and styrene) at a concentration of 50 ng mL⁻¹ (DI) and 100 ng mL⁻¹ (HS). Samples were maintained in amber glass bottles without headspace and in the dark for 24 h until analysis. The samples were all run in triplicate (n=3) and the relative error (RE) calculated for each sample. The overall accuracy was assessed by subtracting the theoretical concentration of each QC sample from the mean concentration determined from the analyses. This difference was then divided by the theoretical concentration and converted to a percentage. Acceptable accuracy was defined as a RE \leq 15. The accuracy of the overall means was ca. < 9 %, which satisfied our acceptance criteria. There are some exceptional cases in which the RE values exceed the ones that are already established. It can be ascribed to the potential interaction that can occur between the analytes and some components of the sample matrix as the samples were not directly analyzed after fortification.

The recovery values (average of three replicates) obtained for each of the fortified samples analyzed are shown in Table 3. As it can be seen, the direct immersion approach showed better accuracy than the HS mode as the percentage of recovery obtained was in all cases higher than 80 %, while the recoveries in the HS modality were lower. The recovery values achieved in the DI configuration fulfill the 70–130 % recovery criterion established by the US-EPA [24], being also an advantage over the HS one. In the light of these results, the DI μ SPE modality can be considered as a valuable alternative for the analytical problem selected.

Conclusions

The role of carbon nanoparticles in (micro)solid phase extraction has been extensively highlighted in the literature but fewer references deal with the use of SWNHs. Our research group has demonstrated their potential in (micro)solid phase

Table 3 Recovery study for toluene, ethylbenzene, xylene isomers and styrene spiked to water samples analyzed following the DI and HS microextraction methods.

Analyte	Direct immersion			Headspace		
	River water (%; n=3)	Tap water (%; n=3)	Bottled mineral water (%; n=3)	River water (%; n=3)	Tap water (%; n=3)	Bottled mineral water (%; n=3)
Toluene	104±10	86±8	101±10	102±10	95±9	90±9
Ethylbenzene	86±5	83±5	99±6	87±9	64±7	50±5
m- and p- xylene	90±4	84±4	99±4	96±10	64±7	84±9
o- xylene	107±4	90±4	91±4	84±11	71±9	48±6
Styrene	104±5	87±4	88±4	104±9	64±6	104±9

Table 4 Comparison of the performance of SWNHs versus other microextraction methods described in the literature for the determination of volatile organic compounds

Extraction methodology	Detection technique	Sample	Sample volume (mL)	Organic solvent/nanosorbent	Elution	LOD (ng·L ⁻¹)	Precision (RSD, %)	Recovery (%)	Ref.
DI- μ SPME	GC-MS	River, tap and bottled mineral water	20	Single walled carbon nanohorns	Hexane	3.5–4.3 (2.5 for toluene)	3.9–9.6 (n=5)	83–107	Proposed method
DI-SPME	GC-FID	Paint wastewater	4.5	Carbon nanotubes reinforced sol-gel	Methanol	0.49–0.61	3.40–5.20 (n=5)	74–87	[25]
DI-SPME	CG-FID	Groundwater	20	Ion pair of cationic surfactant (CTAB) and tungstosilicic acid	Thermal desorption	0.22–5.61	1.48–4.27	–	[26]
HS- μ SPME	GC-MS	River, tap and bottled mineral water	20	Single walled carbon nanohorns	Hexane	120–138	8.7–13.3 (n=5)	50–104	Proposed method
HS-SPME	GC-FID	Paints	20	Ionic liquid	Thermal desorption	0.1–0.8 ($\mu\text{g}\cdot\text{mL}^{-1}$)	3.50–10	70–109	[27]
HS-SPME	CG-FID	Tap and river water	5	Polypropylene hollow fiber membrane	Thermal desorption	110–370	1.18–3.70 (n=4)	–	[28]
HS-SPME	CG-FID	Waters	10	Polymetric fullerene	Thermal desorption	1.40–2.50	3.50–8.83	–	[29]

extraction technique either dispersed in the sample matrix or supported on a microporous hollow fiber. Up to now, no evaluation of their use in headspace/direct immersion has been carried out.

In this paper, the performance of o-SWNHs immobilized on the pores of a hollow fiber under the headspace and direct immersion modalities has been compared. For this purpose, volatile pollutants, namely toluene, ethylbenzene, xylene isomers and styrene have been selected as target analytes.

The study carried out in this paper demonstrated that the direct immersion modality is again the best approach even for the determination of very volatile compounds such as toluene, ethylbenzene, xylene isomers and styrene. Maybe, the most critical variable affecting to the HS approach is the main reason behind this result as it was not possible to work at temperature below 20°C. The use of lower temperature would have improved the analytical figures obtained. In spite of this limitation, the results obtained point out that the microextraction unit can isolate the volatile organic compounds although with a lower sensitivity. This is the first time that this unit is evaluated under this modality which would be useful for the determination of these compounds in more complex samples such as petrol, olive oil or soils. Concerning the DI-o-SWNHs-HF μ SPME, the sensitivity was adequate to determine the selected analytes in water samples, with preconcentration factors between 12.33 and 34.13. These values could be better if the chemical elution of the analytes from the fiber would have been changed by the thermal desorption in the injector of the gas chromatograph. An improvement in this modality will be afforded in future works. The main limitation of the HS modality, the low sensibility, will also be studied in future work as it is a valuable alternative for the determination of volatiles compounds in solid and dirty liquid samples.

The extraction unit works under the solid-phase extraction principles as no organic solvent or aqueous media are added as coadjuvants of the extraction process. This is a clear difference with other extraction approaches based on the use of hollow fiber, in which the liquid phase microextraction format is preferred. Table 4 compares the performance of the DI and HS μ SPME modalities for the determination of the target compounds in liquid samples. The use of reinforced carbon nanotubes sol-gel SPME is more sensitive than the proposed approach although the amount of nanoparticles used is higher. Despite this negative comparison, our alternative is simpler in terms of fiber preparation and the microextraction unit can be reused several times without carry over between samples or efficiency losses. In addition, the LODs reached with the carbon nanohorns immobilized on the porous fiber are low enough to analyse water samples according the legislated limits. As far as headspace modality is concerned, the use of o-SWNHs hollow fiber is not competitive as many of the alternatives use thermal desorption which is in fact more

sensitive than the chemical elution as no analyte dilution occurs after preconcentration on the solid support.

Acknowledgements Financial support from the Spanish DGICYT (Grant CTQ2011-23790) is acknowledged.

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