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Solid phase (micro)extraction tools based on carbon nanotubes and related nanostructures

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1. Introduction

The evolution of Analytical Sciences has been marked by several turning points which have changed the analytical laboratories. They have defined a variety of stages dominated by one or two key trends in Analytical Chemistry with clear influence in the “products” yielded in those years. This evolution started with the massive use of instruments in 1950s and continues with the growing importance of miniaturization and simplification in recent years. Nowadays, the analytical trends are also influenced by the development in other scientific and technological areas. Concretely, nanotechnology can be considered as a new, increasingly important trend in science in general and in analytical chemistry in particular. The outstanding properties of the nanoparticles and nanostructured materials have opening up a wide variety of challenging possibilities in this area. It should be expected that the evolution of this analytical trend will be markedly affected by the nanotechnological developments.

Nowadays there are a large variety of nanoparticles commercially available or easily synthesizable in the laboratory such as gold nanoparticles, quantum dots and carbon nanoparticles, among others. Carbon nanotubes (CNTs) have received special research attention since their discovery on account of their unique and outstanding properties which results in a wide variety of applications in different scientific and technological areas.

Carbon nanotubes can be considered as a graphene sheet that has been rolled up to form as extended tube-like structures (Harris, 1999). They range between a few tens of nanometers and several micrometers in length with an outer diameter from ca. 2.5 to 30 nm. They can consist of a single graphene sheet (singlewalled carbon nanotubes, SWCNTs) or a series of concentric layers (multiwalled carbon nanotubes, MWCNTs).

Since their discovery in 1991 by Iijima (Iijima, 1991), carbon nanotubes have been the target of theoretical and practical research with the aim of elucidating their outstanding properties at the nanoscale level. The main difficult in this context is the marked tendency to aggregation of this nanomaterial, which makes difficult to distinguish between supramolecular assemblies and isolated carbon nanotubes properties. Apart from their thermal stability, excellent mechanical and electric properties, as well as their highest tensile

strength among known materials, three characteristics which will play a crucial role in their sorption capacity can be highlighted (Valcárcel et al., 2007):

- They present nonpolar bonds and high length to diameter ratio. This results in a low water and commonly used organic media solubility and high aggregation tendency in these media as a result. This negatively affects the effective surface area available for interactions with analytes.
- They can be covalently functionalized. Although they are not especially reactive, they can incorporate hydroxylic or carboxylic groups on their side walls under strong chemical conditions. It permits the immobilization of carbon nanotubes on solid supports such as controlled pore glass, silica or steel.
- They can establish non-covalent interactions with analytes which include hydrogen bond, π - π stacking, dispersion forces, dipole-dipole interactions and hydrophobic effect.

2. Sorbent properties of carbon nanotubes

As it has been commented on, the hydrophobic surface of carbon nanotubes permits the establishment of strong interactions with organic compounds. Indeed, several examples can be found in the literature dealing with the use of carbon nanotubes as effective sorbents in water treatment as regards octadecyl silica (RP-C18) or activated carbon (Liu et al., 2004) (Pyrzynska et al., 2007). Recently an excellent critical review dealing with the adsorption mechanisms of organic chemicals on carbon nanotubes have been published (Pan & Xing, 2008a). The authors stated in their article that the chemical adsorption on carbon nanotubes cannot be easily described using a single adsorption model. It can be ascribed to the fact that the presence of surface defects, functional groups or even interstitial regions can generate preferential adsorption sites. Readers interested in a detailed explanation on these mechanisms are referred to the article by Pan and Xing. Initially, the hydrophobic interactions between the carbon nanotubes surface and the organic analytes were considered as the sole mechanism for adsorption. If this is so, the interactions can be predicted by means of the octanol-water distribution constant, K_{ow} . However, further investigations demonstrated that it was not possible to establish an explicit relationship between the adsorption coefficient of the organic compounds and the corresponding K_{ow} value (Chen et al., 2007) (Pan et al., 2008b). Three additional mechanisms have been proposed to explain the adsorption of the analytes on the carbon nanotubes such as the π - π interactions that can be established between the aromatic moiety of the molecule and the π -system of the nanotubes; the hydrogen bonds with the functional groups of the nanostructures; and electrostatic interactions due to the residual charge on the nanotubes surface (Lin & Xin, 2008) (Chen et al., 2008). As several factors affect these interactions, the relative contribution of each mechanism cannot be easily attributed.

Probably, one of the variables that will determine the availability of the adsorption equilibrium is directly related to the carbon nanotubes properties, viz: aggregates and functional groups. Moreover, the chemical environmental conditions (e.g. pH, ionic strength and surfactants) can also affect the analyte-CNTs adsorption.

The insolubility of carbon nanotubes in common aqueous and organic media results in the formation of aggregates of different sizes and stability. As a result, the superficial sites available for analytes interaction decreased as, the interstitial and inner pores adsorption is sterically hindered. The procedure selected for the synthesis of the carbon nanotubes can also influence the adsorption capability of the material as residues of amorphous carbon and metal catalyst could also block the inner pores (Yang et al., 2006).

Different procedures have been described to reduce or even eliminate these negative effects on analytes adsorption. The sorbent capacity of surfactant coated carbon nanotubes has been deeply studied in the literature (Carrillo-Carrión et al., 2007a). This evaluation was conducted using toluene and n-undecane as model compounds for the calculation of the corresponding solid-liquid and liquid-liquid isotherms. In order to obtain relevant conclusions, solid-liquid single component isotherms were calculated under three different experimental conditions: solid multiwalled carbon nanotubes; surfactant coated carbon nanotubes and surfactant media (sodium dodecyl sulphate, SDS). In all cases, the concentration of the nanoparticles and surfactant were maintained constant. For the liquid-liquid isotherms, the distribution of the analytes between an organic solvent (heptane) and an aqueous phase containing solid nanotubes, surfactant coated nanotubes and surfactant was considered.

The behaviour observed for the solid-liquid and liquid-liquid isotherms was analogous. The authors concluded that the maximum extractant capacity for toluene corresponds to dispersed nanotubes, with negligible contribution of the SDS solution. This fact permits one to assess that the whole adsorption can be attributed to the presence of the carbon nanoparticles. If benzene is considered instead of toluene as analyte, the enrichment factor obtained is lower which can be explained by the fact that the presence of methyl group in the toluene molecule would facilitate the adsorption on the MWCNTs surface due to an additional interaction with the hydrocarbon chain of the surfactant. On the contrary, the n-undecane extraction was maximum with the surfactant, with the lowest yields obtained with non-dispersed carbon nanotubes. The hydrocarbon molecules are located in the core of the micelles, and when surfactant coated carbon nanoparticles are used, there are fewer sites available, which reduces the extraction efficiency. However, the n-undecane can substitute the carbon nanoparticle from the micelles as the stability of the suspension is lower, providing an intermediate extraction capability.

From the above, it can be concluded the adsorption properties of carbon nanotubes are affected by the nanoparticles state, being possible to increase this property by the use of surfactant, which clearly reduces the natural aggregation tendency of these nanoparticles, increasing the active surface of CNTs.

Adsorption of organic compounds on carbon nanotubes can also be affected by the synthesis procedure and further purification step. The raw material is mainly hydrophobic and in general, the adsorption can be increased after heating the carbon nanotubes due to the removal of amorphous carbon and oxidation of residual catalyst moieties. The increasing amount of oxygenated groups will lead to a higher interaction with polar compounds due to an increased hydrophilicity of the carbon nanotubes. Other functional groups such as -OH, -COOH and -CO can be added by acid treatment (typically a mixture of HNO₃ and H₂SO₄). The presence of these moieties can be used for carbon nanotubes immobilization on a variety of surfaces. The presence of isolated nanostructures can increase the adsorption

through a reduced aggregation. Finally, the hydrophobicity of the carbon nanotubes can be restored by using extreme heating conditions (viz 2200 °C).

Depending on the conditions used, the most appropriated carbon nanotubes state can be selected for the given application. The next sections are devoted to the reported applications of carbon nanotubes and related materials in solid phase (micro) extraction.

3. Carbon nanoparticles in solid-phase extraction

Solid-phase extraction (SPE) is a well-known, worldwide used sample treatment technique. Its favourable features as regards analytes preconcentration factors, interferences removal, solvent consumption, sample processing time, automation and potential sorbent reusability, justifies its use against its counterpart liquid-liquid extraction. Moreover, the variety of sorbents currently available permits the preconcentration of analytes of different polarity and even charged species.

Among the new sorbents proposed for SPE, carbon nanostructures and more specifically fullerenes and carbon nanotubes have been successfully used in this context (Valcárcel et al., 2008). The applicability of these nanoparticles in this separation technique relies on the sorbent properties described in the previous section of this chapter. Here, the main applications of carbon nanostructures in SPE will be presented. The selected examples have been classified according to the extraction unit in which the nanoparticles can be presented, namely, commercial cartridges and minicolumns. Furthermore, their used immobilized on a solid support and dispersed with surfactants will be commented on.

Carbon nanotubes have been used packed in conventional SPE cartridges for the determination of a variety of organic compounds in different matrices. The isolation and preconcentration of organic pollutant from environmental samples is the most reported application of this configuration. By way of sample, Table 1 lists analytical information related to these references.

Sample	Analyte	Amount of sorbent	Sample volume	Eluent	Detection technique	Reference
Environmental waters	4-n-nonylphenol 4-tert-octylphenol	500 mg MWCNTs	500 mL	MeOH, 2.5 mL	HPLC-FL	Cai et al., 2003
Environmental waters	Chlorophenols	300 mg MWCNTs	200 mL	MeOH, pH 10, 6 mL	HPLC-UV	Cai et al., 2005
Environmental waters	Atrazine Simazine	100 mg MWCNTs	500 mL	ACN, 4 mL	HPLC-DAD	Zhou et al., 2006a
Environmental waters	Cyanazine Chlortoluron Chlorbenzuron	100 mg MWCNTs	250 mL	CH ₂ Cl ₂ , 5 mL	HPLC-UV	Zhou et al., 2007a
Waters	Sulphonylurea Herbicides	100 mg MWCNTs	500 mL	ACN 1% acetic acid, 12 mL	HPLC-DAD	Zhou et al., 2007b
Waters	Dichlorophenyltrichloroethane and metabolites	100 mg MWCNTs	500 mL	CH ₂ Cl ₂ , 5 mL	HPLC-UV	Zhou et al., 2006b
Pork	Barbital, amobarbital and phenobarbital	250 mg MWCNTs	10 mL	Acetone:Ethylacetate 3:7 (v:v), 5 mL	GC/MS/MS	Zhao et al., 2007
Urine	Antidepressants	30 mg MWCNTs	10 mL, diluted in water 1:1	ACN:acetic acid 97:3, 2 mL	HPLC-UV	Cruz-Vera et al., 2008
Virgin olive	Pesticides	30 mg c-SWCNTs	3 mL, diluted in water 1:1	Ethylacetate, 0.5 mL	GC-MS	López-Feria et al., 2009

Table 1. Main analytical features of the procedure developed using carbon nanotubes packed cartridges.

The first sign of the adsorption capacity of carbon nanotubes was revealed by Long et al. (Long & Yang, 2001) when they proposed their use for dioxin removal. Two years later, the first analytical application of packed carbon nanotubes was reported (Cai et al., 2003). The authors employed a commercial polypropylene SPE cartridge from which the sorbent was replaced by 500 mg of multiwalled carbon nanotubes. The upper and low frits were maintained at both ends to hold the nanotubes in place during the extraction. The cartridge was evaluated for the enrichment of bisphenol A, 4-n-nonylphenol and 4-tert-octylphenol from waters. The high affinity of the carbon nanotubes for the endocrine disruptors is demonstrated by the large volume of sample that can be preconcentrated (up to 1 L) without analytes losses. Moreover, the low volume of organic eluent required (2.5 mL of methanol) permits limits of detection as low as 0.018 ng/mL (for 4-n-nonylphenol). The analytical figures of merit provided by the nanostructured material resulted better than those of RP-C₁₈ and XAD-2 for these compounds. The applicability of carbon nanotubes to solve environmental-related analytical problems was extended in the following years by determining chlorophenols (Cai et al., 2005), herbicides (Zhou et al., 2006a) (Zhou et al., 2007a) (Zhou et al., 2007b) and dichlorodiphenyltrichloroethane and metabolites (Zhou et al., 2006b) in waters. In all cases, multiwalled carbon nanotubes were preferred to singlewalled carbon nanotubes as the presence of concentric sheets resulted in an enhanced interaction with the analytes. The amount of sorbent used can be reduced to 100 mg and in some of the applications, the cartridge can be reused up to 200 times without efficiency loss (Zhou et al., 2007a). The eluent used was different depending on the analyte and, in some cases the use of mixtures is needed. Moreover, the eluent volume required for quantitative elution can be as high as 6 mL which is an inconvenience for sensitivity. An evaporation-redissolution step can be used to overcome this limitation.

In addition to waters, the use of commercial cartridges packed with MWCNTs has been extended to the determination of barbiturates in porks (Zhao et al., 2007), antidepressants in urine (Cruz-Vera et al., 2008) and pesticides in virgin olive oil (López-Feria et al., 2009). In the last two articles, the amount of carbon nanotubes was reduced to 30 mg and, despite the matrix complexity, the cartridge reusability was demonstrated by the authors by the mere inclusion of a washing step between samples.

Recently, a novel carbon nanostructure, carbon nanocones, has been proposed for its use in SPE cartridge (Jiménez-Soto et al., 2009). The commercial product contains 20%wt carbon nanocones, 70%wt carbon disks and 10%wt amorphous carbon. The presence of the amorphous solid results in irreversible interactions with the analytes and lower recovery values, as result. This negative effect can be reduced by maintaining the commercial solid at 450 °C for 20 min. This treatment dramatically reduced the amorphous carbon content with negligible influence on the nanostructured material. In the model application developed for the determination of chlorophenols in waters, 20 mg of the thermally treated sorbent were packed in a 3-mL commercial SPE cartridge. Limits of detection as low as 0.3 ng/mL were achieved by preconcentrating 2 mL of water sample and eluting the retained compounds with 200 µL of hexane. As compared with carbon nanotubes, the conical nanostructures showed to be more efficient in the preconcentration process as similar analytical features were obtained with lower sorbent amount. This fact can be explained taking into account that the carbon nanocones show lower aggregation tendency than the carbon nanotubes and, therefore, the effective surface available for analytes interaction is higher with the former.

Solid-phase extraction has also been implemented in a continuous fashion by using flow system configurations. This approach permits the miniaturization and automation of the whole process with the inherent advantages. Fullerenes have been extensively used in this context. The general configuration used is depicted in Figure 1. As can be seen, an amount of ca. 80 mg of fullerene C₆₀ are packed in a PTFE minicolumn fitted with cotton wool beds at both ends to prevent sorbent losses. The column is placed in the loop of an injection valve to allow the preconcentration of large volumes of sample. Once the sample has been completely aspirated into the system, a small plug of eluent (in the microliter range) was passed through the C₆₀ column for analytes elution. As the continuous unit is on-line coupled to the atomic absorption spectrometer, a transient analytical signal is obtained when the eluent, containing the analytes, reach the flame. By using this configuration, a large variety of metals and their alkyl derivatives have been determined in waters. Table 2 summarized the main applications developed in this context. As can be seen, the adsorption capacity of fullerene C₆₀ for organic compounds is rather limited while they show great potential retaining organometallic compounds. The study carried out by Ballesteros et al. (Ballesteros et al., 2000) also pointed out that the efficiency of the extraction process decreased when the polarity of the analytes increased. Despite this behaviour, some references dealing with the determination of organic molecules using fullerenes as sorbent have been reported. Serrano et al. used fullerene C₆₀ for the extraction of benzene, toluene, ethylbenzene and xylene isomers from waters (Serrano & Gallego, 2006). In this case, the preconcentration step was followed by the gas chromatographic-mass spectrometric determination of the volatile organic compounds. The sensitivity and precision of the method were better than those obtained with conventional sorbents such as RP-C18 and Tenax TA. Moreover, the selectivity was also enhanced as fullerenes were not affected by the low pH selected for retention. As far as metallic species is concerned, they required previous derivatization to form neutral chelates that could be effectively retained on fullerenes. In order to obtain discriminated information on the sample composition, a chromatographic separation can be implemented after the analysis of the sample by an atomic technique to estimate the total concentration of the target metals in the sample. Such is the case of the determination of lead and alkyllead compounds in rainwaters (Baena et al., 2000) or organometallic compounds in environmental samples (Muñoz et al., 2005).

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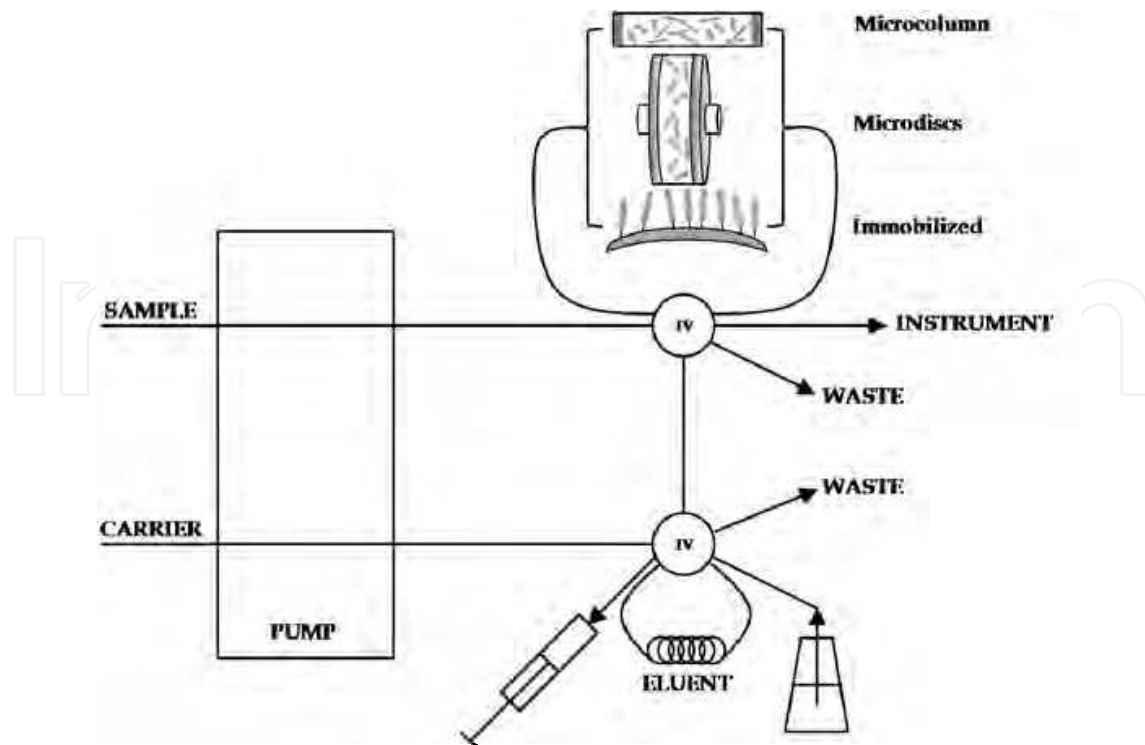


Fig 1. Flow configuration for the use of carbon nanotubes as sorbent in solid phase extraction procedures.

Sample	Analyte	Sorbent	Eluent	Instrumental technique	Reference
Environmental samples	Cd, Mn, Ni	MWCNTs	HNO ₃ 0.1 M	ICP-AES	Liang et al., 2004
Waters	Cu	MWCNTs	HNO ₃ 0.5 M	FAAS	Liang et al., 2005
Egg and pork	Sulfonamides	MWCNTs	Mobile phase MeOH:H ₂ O 22:78	HPLC-UV	Fang et al., 2006
Waters	Pb (II)	c-MWCNTs	HNO ₃ 1 M	FAAS	Barbosa et al., 2007
Waters	BTEXs	Fullerene C ₆₀	Ethyl acetate	GC-MS	Serrano & Gallego, 2006
Waters	Pb	Fullerene C ₆₀	IBMK	FAAS	Gallego et al., 1994
Wheat flour	Co	Fullerene C ₆₀	IBMK	ETAAS	González et al., 1999
Rainwaters	Pb and alkyllead derivatives	Fullerene C ₆₀	IBMK	FAAS	Baena et al., 2000

Table 2. Representative examples of the applicability of carbon nanotubes and fullerenes in continuous flow separation techniques.

Reducing the dimensions of the extraction units for carbon nanotubes was also aimed at minimizing the aggregation of the nanoparticles which negatively affects to the retention efficiency. Therefore, Suárez et al. proposed the package of 6 mg of MWCNTs in the minicolumn, which was further located in the loop of the injection valve. It permits the retention and elution processes to be carried out in opposite direction thus reducing the compacting of the sorbent. This approach has been used for the determination of tetracycline residues in waters (Suárez et al., 2007a). In this case, the minicolumn presents a

larger diameter, (9 mm i.d.) than that reported for fullerenes, which also helps to reduce the overall pressure in the system. A similar configuration has been on-line coupled to a liquid chromatography for the simultaneous determination of 10 sulfonamides in egg and pork (Fan et al., 2006).

Suárez et al. used immobilized carboxylated singlewalled carbon nanotubes (c-SWCNTs) on inert controlled pore glass and used the combined solid as sorbent in SPE (Suárez et al., 2007b). An accurately weighed amount of 15 mg of the combined solid was packed in a PTFE tube (1.2 mm i.d.) which was placed in a continuous flow device. The automated system was used for the determination of non steroidal anti-inflammatory drugs (NSAIDs) in urine samples. The authors compared the adsorption capacity of the same amount of immobilized c-SWCNTs, SWCNTs and MWCNTs for tetracyclines and NSAIDs [Figure 2]. The best results were obtained with the immobilized sorbent, with the additional consideration that the amount of nanoparticles is lower than in the other cases as the weighed material refers to both, the c-SWCNTs and the inert glass. It can be ascribed to the fact that the immobilization process results in a vertical alignment of the c-SWCNTs on the particle surface, which clearly enhanced the molecular interactions of the analytes with the nanotube surface.

The determination of inorganic species using carbon nanotubes requires the previous derivatization of the nanoparticles to introduce functional groups (carbonyl, carboxylic and hydroxyl) that allows the interaction with the metallic species. Such is the case of the extraction of cadmium, manganese, and nickel (Liang et al., 2004), Cu (II) (Liang et al., 2005) or Pb (II) (Barbosa et al., 2007) from waters. In these applications, the pH of the sample resulted to be a critical variable as it will define the surface charge of the sorbent, which should be negative to interact with the cations. The microcolumns of variable dimensions and containing an average sorbent amount of 50 mg were inserted in a continuous flow configuration that can be on-line coupled to the flame atomic absorption or inductively coupled plasma atomic emission spectrometers.

As it was indicated in the previous section, surfactants have been reported to disperse carbon nanoparticles in aqueous media, facilitating their use for analytical purposes. The aqueous suspension obtained is stable under optimal conditions (the amount of nanoparticles and surfactant concentration being critical) as the nanoparticles are located inside the micelles. The surfactant coated carbon nanoparticles have been used as pseudophase for liquid-liquid extraction (Carrillo-Carrión et al., 2007a). The interactions between the organic compounds and the dispersed carbon nanotubes differ from that observed for the raw material. As no aggregates exist in the dispersed phase, more adsorption sites are available for retention, which has a positive effect on extraction. This methodology has been successfully applied for the extraction of benzene, toluene, ethylbenzene and xylene isomers from olive oil samples with a clearly sensitivity and selectivity enhancement in comparison with the direct headspace analysis (Carrillo-Carrión et al., 2007b). The procedure is schematically depicted in Figure 3.

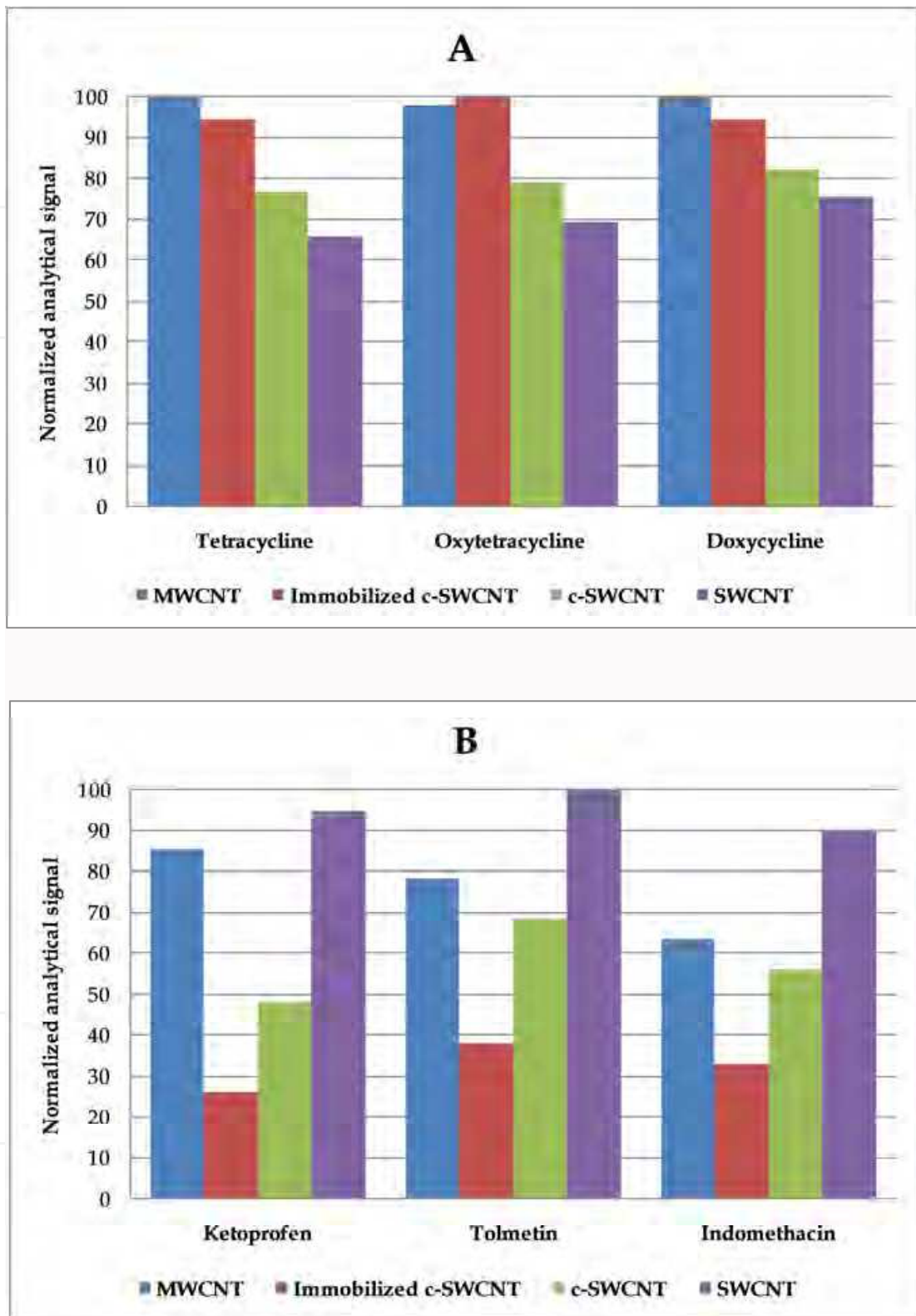


Fig. 2. Comparison of sorption capacity of different types of carbon nanotubes

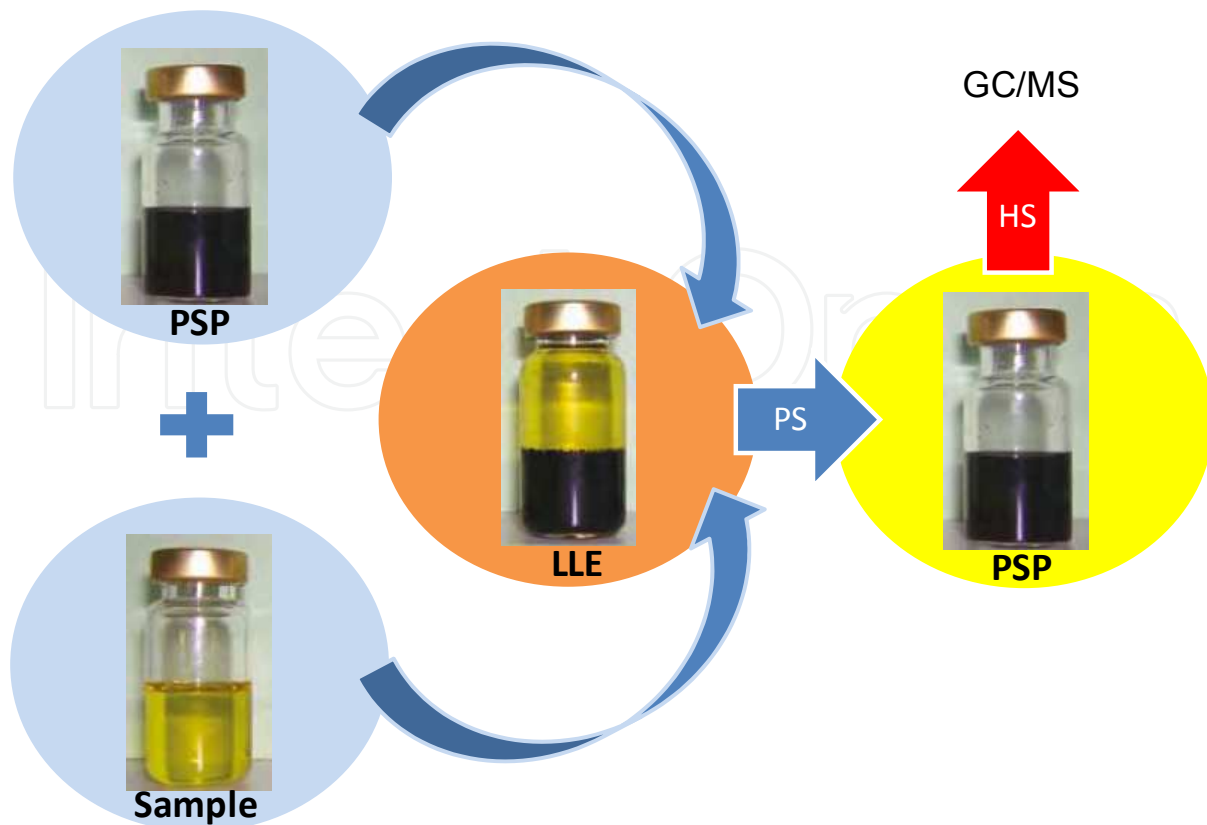


Fig. 3. Analytical procedure for the liquid-liquid extraction (LLE) of BTEXs from olive oil samples using surfactant coated nanotubes as pseudophase (PSP)

Finally, and considering the thermal stability of the carbon nanotubes, they can be used as preconcentration units on-line coupled to a gas chromatograph for retention of low molecular weight compounds (methyl-ethyl ketone, toluene and dimethyl methyl phosphonate) from a vapour stream by maintaining the unit at low temperature. For desorption, the temperature was rapidly increased and the analytes directly transferred to the injection port of the instrument (Zheng et al., 2006).

4. Solid phase microextraction based on carbon nanoparticles

Solid-phase microextraction (SPME) appeared as an evolution of the solid phase extraction. It was introduced by Arthur and Pawliszyn in 1990 (Arthur & Pawliszyn, 1990) and it was conceived as an alternative to traditional methods for sample preparation. SPME overcomes the main drawbacks of classical preconcentration techniques, regarding the number of steps involved, extraction time or the consumption of toxic organic solvents. Solid-phase microextraction has gained importance in recent years because it is an efficient and fast methodology which combines in a single step, the sampling, preconcentration, matrix removal and injection in the chromatographic system. Owing to its favourable features, SPME has widely been applied in various fields including environmental, food, natural products, pharmaceutical, biology, toxicology and forensic (Pawliszyn, 1999).

SPME is based on the distribution of the analytes between the sample (or its headspace) and the stationary phase immobilized on the solid support. The analytes transference starts

when the coated fiber is placed in contact with the sample and it is considered that the extraction is complete when the equilibrium between the sample matrix and fiber coating is reached (Pawliszyn, 1997).

The SPME extraction process can be carried out in three ways: direct-immersion, headspace configuration, and membrane-protected approach (Pawliszyn, 1997). In the direct-immersion method (DI-SPME), the coated fiber is completely immersed in the sample matrix (liquid or gas) and the analytes are directly transferred to the extractant phase under continuous stirring. In DI-SPME, the selectivity is provided by the type of fiber coating, the main limitation being the potential fiber damage due to irreversible interaction with endogenous matrix compounds. In headspace mode (HS-SPME), the analytes are released from the sample matrix to its headspace for further interaction with the coating of the fiber. The selectivity of this approach is higher and the fiber lifetime longer, although it is limited to the preconcentration of volatile analytes. The membrane-SPME approach permits the isolation/enrichment of polar compounds from aqueous samples by protecting the polar probe by means of an hydrophobic membrane. It can expand the applicability of the SPME with the additional selectivity enhancement provided by the membrane (Pawliszyn, 1997). Once the analytes have been preconcentrated on the fiber coating, the next step is their desorption for qualitative and quantitative analysis. The thermal desorption is the preferred choice taking into account that the compounds are separated by gas chromatography. In this case, the analytes are transferred to the chromatographic column by heating the fiber in the injector of the instrument. It reduces the analytes dilution with the favourable effect on the sensitivity. For the HPLC coupling, the analytes are eluted by means of the proper organic solvent/mobile phase.

The type of coating used in the SPME fiber plays a crucial role in the extraction/desorption process, since the efficiency of this process will depend on the distribution constant between the analytes and the stationary phase. In addition, it will provide some selectivity to the SPME process towards the analytes versus other matrix compounds. For this reason, a wide variety of materials are used as coatings for SPME fibers. The most common commercially available are: polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), Carbowax (CW) and Carboxen. Despite their advantages, they also present some drawbacks regarding the instability at high temperatures (e.g 240-280 °C), which results in the presence of artifacts in the chromatogram, carry over owing to incomplete desorption or shorter lifetime of the fiber. Furthermore, the organic nature of the coatings are incompatible in some cases with the use of organic solvents under which the commercial fibers are unstable and have swelling, which reduces or limits their applicability in liquid chromatography. In addition, commercial fibers have poor reproducibility, are fragile and expensive. Therefore, the development of novel coatings for SPME fibers is welcome. The carbon nanostructures have emerged in the last decade as a robust alternative to commercial coatings on account of their excellent mechanical, electrical and chemical properties. Both, fullerenes and carbon nanotubes as well as their derivatives have been used in this context using different immobilization processes. The most relevant reported applications are summarized in Table 3 and they will be commented on.

Sorbent (film thickness, μm)	Analytes	Sample type	LOD (ng/L)	Precision (% RSD)	Recoveries (%)	Reference
MWCNT (40)	PBDEs	River water and milk	3.6-8.6	6.9-8.8 (n=4)	90.0-119.0	Wang et al., 2006
MWCNT (35)	PBDEs	Water	1.1-16.2	5.0-9.1 (n=5)	74.2-98.7	Tian & Feng, 2008
c-MWCNT (20)	Phenols	River and wastewater	5.0-50.0	0.97-7.96 (n=3)	70.83-148.10	Liu et al., 2009
SWCNT (50)	OCPs	Lake and wastewater	0.19-3.7	3.5-13.9 (n=5)	44.7-111.0	Lü et al., 2007
SWCNT (50)	Oxygenated ethers	Human urine	10.0	4.8-9.6 (n=6)	90.0-95.0	Rastkari et al., 2009
c-MWCNT/MWCNT (50)	Phenols	River and wastewater	0.25-3.67	1.52-6.38 (n=5)	86.13-118.64	Liu et al., 2007
MWCNT (12.5)	Polar aromatic compound	Water	30.0-570.0	4.4-7.5 (n=7)	83.3-106.0	Chen et al., 2009
MWCNT	Aromatic hydrocarbons	Petrol station wastewater	90.0-390.0	4.8-9.6 (n=6)	93.8-106.1	Adomaviciute et al., 2008
c-MWCNTs (3)	BTEX	Water	-	1.8-2.5 (n=6)	-	Jiang et al., 2009
c-SWCNT (25)	Phenols	Sea and tap water	900.0-3800.0	0.7-3.2 (n=3)	87.5-102.0	Li et al., 2009
MWCNT (40)	Phenols	Water	1.0-65.9	2.7-6.5 (n=6)	87.7-115.5	Du et al., 2009
Polymeric fullerene (33)	Aromatic hydrocarbons	Water	80.0-1200.0	1.52-6.80 (n=6)	-	Xiao et al., 2001
Hydroxyfullerenes (30)	Aromatic hydrocarbons	Water	0.013-125.0	1.1-8.9 (n=6)	88.2-94.0	Yu et al., 2002

Table 3. Selected applications on the use of carbon nanoparticles as active components in SPME.

Carbon nanotubes have been immobilized on the SPME fiber by physical deposition technique or dipping technique, which consists in the immersion of the uncoated fiber into a solution of the sorbent material for a short period of time, and subsequent solvent removal by evaporation. Wang et al. (Wang et al., 2006) used a fused silica fiber without the polyimide protective layer as probe support. It was then immersed in a dimethylformamide solution containing MWCNTs at a concentration of 20 mg/mL. The organic solvent was further removed by heating at 160 °C. The process was repeated until the desired coating thickness was reached, in this case, ca. 40 μm . Later, the fiber was subjected to a sintering process by heating at 80 °C for 30 min, further increasing the temperature to 280 °C for 4 h, under an helium stream. Finally, the fiber was assembled on a modified syringe to be used as SPME device for the determination of polybrominated diphenyl ethers (PBDEs) in milk and water samples by gas chromatography (GC) with electron-capture detection (ECD). The SPME process was carried out by direct immersion of the fiber in the samples and the thermal desorption in the gas chromatograph injector at 295 °C. The fiber-to-fiber reproducibility expressed as relative standard deviation (RDS) ranged between 8 to 16 %, using three fibers coated with the same procedure. Furthermore, the fiber could be used up to 100 times with negligible loss of performance. Also, a comparison with other coatings, namely activated carbon and poly (5% dibenzene-95% dimethylsiloxane) (PDMS-DB) was carried out following the same coating and SPME procedures. The results were compared through the enrichment factor (EF), defined as the ratio between the peak area after extraction and the peak area of the direct injection of a standard solution. The comparison pointed out that the MWCNTs coating reached enhancement factors 4 to 4.5 times higher than activated carbon and PDMS-DB. In the same way, Tiang and Feng (Tiang & Feng, 2008)

carried out a similar process for SPME fiber coating with MWCNTs for the determination of polybrominated diphenyl ethers (PBDEs) in water samples. In this case, the extraction process was carried out using the DI-SPME (20 °C, 45 min) and HS-SPME (100 °C, 45 min) approach. As a result, the analytical response obtained with the HS-SPME was better (between 2-4 times) with cleaner chromatograms and longer fiber lifetime. Moreover, the precision (RSD, $n = 5$) ranged between 5.0% and 9.1%. Also, the MWCNTs fiber was compared with the SE-54 coating and it was obtained a sensitivity 3-5 times higher for the MWCNTs. It can be ascribed to the large specific surface and strong adsorption capability of the nanostructured material. In this context it should also be mentioned the work carried out by Liu et al. (Liu et al., 2009) in which, oxidized MWCNTs were immobilized on a fused silica capillary previously silanized. MWCNTs were functionalized by acid attack ($\text{H}_2\text{SO}_4/\text{HNO}_3 = 3 / 1$) and subsequently dispersed in an aqueous solution with SDS (1%). The fused silica capillary was immersed in the solution of MWCNTs at 70 °C for 4 h and then, dried in an oven at 120 °C. As in the previous cases, this process was repeated until reaching the desired thickness (in this case, 20 μm) and then the fiber was subjected to a sintering process (280 °C, 12 h) under a nitrogen stream. The extraction of selected analytes was made by DI-SPME and subsequent thermal desorption in the injector of the chromatograph. From this work is remarkable precision of the method (RSD, $n = 3$) ranged between 0.97% and 7.96%.

Fullerenes and carbon nanotubes have also been immobilized on the fiber following the epoxy-glued solid sorbent or pasting with adhesives procedure. The coating is accomplished by means of an organic binder. For this aim, both the carbon nanoparticles and the organic binder components are dissolved in a solution in which the support is immersed as many times as necessary to achieve the desired thickness of the coated fiber. Then, the organic solvent is removed and a sintering process is carried out. This simple and expeditious procedure results in a very temperature resistant fiber. The main drawback is the progressive loss of sorbent when the fiber is in contact with organic solvents. In addition, the fiber coating process results in a lower reproducibility between fibers than the physical deposition. Notwithstanding this, the procedure has been successfully used for a variety of applications. Lü et al. (Lü et al, 2007) immobilized SWCNTs on a SPME fiber using an organic adhesive composed of terpineol, ethylcellulose and dibutyl phthalate. Once the fiber was coated, it was used to extract eight organochlorine pesticides in lake and wastewater samples by DI-SPME mode. The precision of the method ranged between 3.5% and 13.9%. Furthermore, a comparison between the SWCNTs fiber and a commercial PDMS one in terms of both thermal stability and lifetime demonstrated that the SWCNTs fiber was better in all instances as it was not affected at temperatures higher than 350 °C and its extraction efficiency remained constant for ca. 150 extractions. This can be explained by the strong adhesion of the coating on the substrate through the organic binding. Rastkari et al. (Rastkari et al., 2009) also used the same compounds to immobilize SWCNTs on a SPME fiber to determine methyl tert-butyl ether, ethyl tert-butyl ether and methyl tert-amyl ether in human urine. Moreover, a similar methodology was implemented by Liu et al. (Liu et al., 2007), who used an epoxy resin to immobilize both raw MWCNTs and functionalized MWCNTs on the fiber. In this work, the desorption method used should be highlighted as it used static desorption mode. For this aim, once the analytes were adsorbed on the SPME fiber, it was placed in contact with an aliquot of 70 μL of acetonitrile:water (70:30 v:v) at room temperature. Then, 5 μL of the solution containing the desorbed analytes was injected

in a HPLC-UV for analysis. The authors demonstrated that the carboxylated-MWCNTs coating provided better responses than raw MWCNTs, Alumina N, Carbograph, PDMS-DVB and CW-TPR. It can be ascribed to the favourable effect of the oxidation process. On the one hand, the acid treatment increases the surface area, which improves the adsorption capacity and the sensitivity of the whole procedure. On the other hand, the functionalized CNTs contain oxygenated groups (COOH, CO, OH) on their surface, which makes the CNTs more hydrophilic, enhancing the affinity for polar molecules. These authors used the same sorbent immobilization technique for to fix carboxylated MWCNTs onto a fused silica capillary, which was further used for in-tube SPME for the determination of substituted aniline compounds in water samples (Liu et al., 2008). The methodology of immobilization by organic glue has also been used by Xiao et al. (Xiao et al., 2001) to fix polymeric fullerenes on a SPME fiber. In this case the immobilization was carried out by dissolving the fullerenes in a solution of heptane containing 5% photosensitive reagent (dicumyl peroxide, DCP) and then, the paste was immobilized by UV radiation. With this modification, the reproducibility between fibers was better than 4% (as relative standard deviation). The coating of CNTs with organic glue or by epoxy resin was also used by Chen et al. (Chen et al., 2009) who used Nafion as the polymer to immobilize MWCNTs on the fiber for the determination of polar aromatic compounds in natural water samples. Similarly, Adomaviciute et al. (Adomaviciute et al., 2008) employed an epoxy glue to deposit CNTs on a modified SPME fiber to determine traces of aromatic hydrocarbons in petrol station wastewaters.

Another technique widely used in the preparation of SPME fibers is the sol-gel approach. In this case, an effective chemical bond is established between the coating and the fiber surface. It clearly improves the thermal stability and resistance of the SPME fiber to organic solvents. However, the reproducibility of the coating procedure is not satisfactory since the method is subjected to a wide number of variables such as pH, temperature and reaction time, concentration and nature of catalyst and sintering step. The sol-gel technique has been used by Jiang et al. (Jiang et al., 2009) to prepare SPME fibers containing CNTs as sorbent. In order to avoid the insolubility of CNTs in some organic solvents, they were functionalized as CNTs-OH and CNTs-COOH derivatives. The steps needed were as follows: first, a stainless steel wire (length 20 cm) was treated with acetone, NaOH and HCl to remove surface impurities. Secondly, the functionalized CNTs were dissolved in a mixture of methyltrimethoxysilane (MTOS), distilled water and poly(methylhydrosiloxane) (PMHS). Later on, the solution was stirred by ultrasound and then trifluoroacetic acid (TFA) was added to form a stable sol solution. To improve the reproducibility in the coating process of the fiber, Jiang et al. used a mechanical device which controls the rate at which the fiber was immersed into the sol-gel solution. In this way, a uniform coating with a controlled thickness was obtained. The fiber was then cut into pieces of 2 cm and it was fixed on a commercial SPME device using epoxy glue. Subsequently, the fiber coated with the sol-gel solution was subjected to a drying process at room temperature for 24 h. Finally, the fiber was conditioned at 50-260 °C under a nitrogen atmosphere for 6 h. The repeatability and reproducibility between fibers was evaluated with an aqueous solution containing BTEX, which were extracted by HS-SPME, obtaining values of repeatability (% RSD, n = 6) and reproducibility (% RSD, n = 5) better than 2.5% and 6.5%, respectively. In terms of reproducibility between fibers, the sol-gel method significantly improves the previously proposed techniques, as a long fiber was initially prepared, and several working fibers were

obtained by cutting the long one into small pieces. Also, the sol-gel-CNT fiber showed a high stability with the temperature, being possible its use at 350 °C. Moreover, a study on the stability of the fiber versus organic solvents such as methanol or acetonitrile was carried out, obtaining a good durability of fiber in these media. Not only carbon nanotubes have been immobilized by the sol-gel technique. This methodology has also been used by Yu et al. (Yu et al., 2002) to deposit hydroxyfullerenes on a fused silica capillary, which was further used for the determination of PCBs, PAHs and polar aromatic amines in water samples by HS-SPME coupled with GC-ECD/FID. The fiber can be used for nearly 200 times, while commercial fibers can be typically used for ca. 40-100 times. Moreover, the coating was stable against temperature (even to 360 °C) and solvents because of the properties of fullerene and the chemical binding between the coating and the fiber surface. Electrochemical deposition is a technique widely used in the field of ceramic materials. It is based on the production of thin film coatings by deposition of charged particles, previously dispersed in an organic solvent, to which an electric field is applied through an electrode. This generates rigid and homogeneous layer on the electrode, which is used as a support of SPME fiber. This is why a support with metallic characteristic such as a steel, aluminum, nickel or titanium fiber is required. The main advantages of using this technique are its simplicity and low cost, easy thickness control, high coating uniformity and compatibility with the use of CNTs. Li et al. (Li et al., 2009) proposed the use of electrophoretic deposition for the coating of functionalized SWCNTs in a SPME fiber. The c-SWCNTs were dispersed in DMF by ultrasonic agitation. Subsequently, two Pt wires (one used as a cathode and another as anode) were immersed in the solution of c-SWCNTs and separated at a distance of 1 cm. A d.c. 40 V was applied between two electrodes for 10 s and the c-SWCNTs were immobilized on the Pt used as anode. Finally, the wire was removed from solution and dried at 120 °C for solvent evaporation. Using this methodology, an homogeneous fiber of 25 µm in thickness was obtained. This SPME fiber was used for the extraction of phenols from water samples by DI mode. Despite the good precision of the method, obtaining RSD values for a single fiber of 0.7-3.2%, the lifetime of the fiber decreased significantly after 80 analyses, which is shorter than that obtained with the organic binder (Lü et al., 2007). In a similar manner, Du et al. (Du et al., 2009) covered a Pt fiber with a composite of MWCNTs and polyaniline (PANI) by electrochemical deposition for the determination of phenolic compounds in lake water samples. For this purpose, a mixture of MWCNTs-PANI was prepared and a Pt wire (which served as a support for fixing the sorbent) was immersed in the supernatant. Subsequently, a electric current varied between -0.1 and 0.9 V at a scan rate of 50 mV/s was applied to the electrode. During electrochemical polymerization, the electrode surface was darkening due to the formation of a thin film of sorbent material. To complete the coating process, the resulting fiber was conditioned under a stream of nitrogen to a temperature of 300 °C for 2 h. The fiber thickness was 40 µm, test by scanning electron microscopy (SEM).

5. Concluding remarks

Analytical Chemistry has benefit from the advanced in other scientific areas such as nanotechnology. The discovery, synthesis and characterization of nanoparticles and nanostructured materials with outstanding properties can be identified as one of the most relevant inputs in this context. Among them, carbon nanoparticles (nanotubes, fullerenes

and nanocones) have been proved to positively contribute to the development of analytical methods with enhanced properties. Their use as sorbent material in different approaches such as conventional SPE procedures, automated flow configurations, pseudophases in liquid-liquid extraction or SPME fibers, has permitted to improve the sensitivity and selectivity of the underlying methods. The reported research has also been capable of reducing or eliminate the negative aspect related to the aggregation tendency of the carbon nanotubes mainly. Although environmental waters have been the most analyzed matrix, some other applications dealing with the analysis of foods and biological sample allows one to advance the future proposal of new approaches in which the carbon nanoparticles, raw or functionalized will play a crucial role.

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This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

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