EFFECT OF SINGLE-WALLED CARBON NANOTUBES ON HYDROXYPROPYL-β-CYCLODEXTRIN STATIONARY PHASE [1]

YIN-XIA CHANG, BING BAI, LI-MING DU, TAO-TAO PANG, YUN-LONG FU*

Analytical and Testing Center, Shanxi Normal University, Shanxi Linfen 041004, PR China
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ABSTRACT

In the present work, we describe a novel application of functionalized single-walled carbon nanotubes (SWCNTs) as a stationary phase for the liquid chromatographic separation of polycyclic aromatic hydrocarbons and structurally similar analogues. The SWCNTs were first oxidized to give carboxylic derivatives (SWCNT-COOH), afterwards these were covalently derivatized with hydroxypropyl-*β*-cyclodextrin (HP-*β*-CD). Then, the HP-*β-CD*-SWCNTs were bonded to silica gel with 3-(triethoxysilyl) propyl isocyanate, which were used as a stationary phase to separate the investigated solutes by HPLC. On this stationary phase, eight polycyclic aromatic hydrocarbons were separated using water/methanol (5:5, *v/v*) as the mobile phase and six structurally similar dipine drugs were also separated using (3:7, *v/v*) methanol/triethylammonium acetate buffer (0.1%, *v/v*, pH 4.1) as the mobile phase. The results showed that the HP-*β*-CD-SWCNTs stationary phase had stronger separation ability for the aromatic hydrocarbons and analogues compared with the HP-*β*-CD stationary phase. This method can be used to improve the separation efficiency of the *β*-CD stationary phases, and the HP-*β*-CD-SWCNTs column can be used for the determination of the aromatic hydrocarbons in wastewater.

Keywords: Carbon nanotubes; HPLC; Stationary phase; Aromatic hydrocarbons; Dipine drugs.

INTRODUCTION

Carbon nanotubes (CNTs) are essentially a sheet of carbon atoms arranged in hexagons that curl into a tube[1]. Possessing unique electrical and electronic properties, high surface area, and good adsorption ability, CNTs have attracted considerable attention in many fields[2]. The intrinsic coupling of electrical properties and mechanical deformation in carbon nanotubes make them ideal candidates for future multifunctional material systems that combine adaptive and sensory capabilities[3]. CNTs also show appealing adsorption properties towards organic and inorganic molecules, and they have potential applications as catalyst supports and probes for drug delivery. The combination of structure, dimensions and topology of CNTs has provided attractive physical and chemical properties that are unparalleled by most known materials[4]. The applications of CNTs have also reached the Analytical Chemistry field in which CNTs are being used as matrices in matrix-assisted laser desorption ionization, capillary electrochromatography, and as pseudostationary phases in capillary electrophoresis electrophoresis, as well as new solid-phase extraction materials[5-8]. In addition, CNTs were incorporated into an organic polymer monolith containing vinylbenzyl chloride and ethylene dimethacrylate to form a novel monolithic stationary phase for HPLC and capillary electrochromatography[9]. A film of CNTs was deposited by chemical vapor deposition (CVD) to form the stationary phase in the open tubular format[10].

CNTs can be functionalized via amidation and esterification of nanotube-bound carboxylic acids. The solubility of these functionalized CNTs makes it possible to characterize and study the properties of CNTs using solution-based techniques[11]. The polymer-based chromatographic stationary phases with embedded or grafted functionalized multi-walled carbon nanotubes (MWCNTs) were prepared and then used to separate materials by HPLC[12]. The surface and adsorption properties of pristine and functionalized MWCNTs were studied as stationary phases for gas chromatographic separation of alkanes and aromatic hydrocarbons[13].

In the recent years, the researh group first reported that functionalized single-walled carbon nanotubes (SWCNTs) were able to assist ionic liquids with enhancing chromatographic characteristics in gas chromatography[14]. The cellulose 2,3-bisphenylcarbamated-SWCNTs or a mixture of cellulose trisphenylcarbamate with the SWCNTs was coated on silica gel as a chiral stationary phase. It was the first time that the SWCNTs have been applied to enantioseparation[15]. The SWCNTs were bonded to 3-aminopropyl silica gel which were used as a stationary phase to separate polycyclic aromatic hydrocarbon with different mobile phases in HPLC[16].

In this work, we show a novel application of functionalized SWCNTs as a stationary phase in the liquid chromatographic separation of the polycyclic aromatic hydrocarbons (PAHs) and structurally similar analogues. With this aim, the SWCNTs were firstly oxidized to give carboxylic derivatives (SWCNT-COOH), afterwards these were covalently derivatized with the hydroxypropyl-*β*-cyclodextrin (HP-*β*-CD). Then the HP-*β*-CD-SWCNTs were bonded to silica gel with 3-(triethoxysilyl) propyl isocyanate, which were used as a stationary phase to separate the investigated substances by HPLC. We found that this stationary phase had stronger separation ability for the PAHs and analogues compared with the stationary phase of HP-*β*-CD. Moreover, the separation ability was also better than that of the SWCNTs bonded silica gel column for the aromatic hydrocarbons.

EXPERIMENTAL

Reagents

Silica gel (particle size 5 μm, pore size 10 nm, specific surface area 400 $m^2.g^{-1}$) was supplied by Lanzhou Institute of Chemical Physics Chinese Academy of Sciences. SWCNTs were purchased from Chengdu Organic Chemistry Co., Ltd, Chinese Academy of Sciences. Hydroxypropyl-*β*-cyclodextrin (HP-*β*-CD) was obtained from Shandong Xinda Fine Chemical CO., ltd (Shandong, China). 3-(triethoxysilyl) propyl isocyanate were obtained from Tokyo Chemical Industry CO., ltd (Tokyo, Japan). Benzene were of analytical reagent grade from Tianjin Kemiou Chemical Co., Ltd. Polycyclic aromatic hydrocarbons were purchased from Aldrich or Fluka and the six structurally similar dipine drugs used in the experiment were obtained from the Chinese National Institute for the Control of Pharmaceutical and Biological Products. Their degree of purity was greater than 99%. Stock standard solutions (100 or 200 $mg.mL^{-1}$) of the analytes were prepared through dissolving them in acetonitrile or methanol and stored at 4°C. in darkness. Solvents used in chromatographic experiments were of HPLC grade. The coke wastewater sample was collected from a Coke Plant in Linfen, China. All other organic solvents and chemical reagents were of at least analytical reagent grade from various commercial sources.

Apparatus

The HPLC analyses were performed using a Waters 1525 binary HPLC pump, a Waters 2489 UV/Visable detector, and a Waters chromatography working station Breeze 2. The detection wavelength was 254 nm. The stainless steel tubes (250 mm×4.6 mm i.d.) (Alltech, USA) were packed with packing materials by a conventional high-pressure slurry packing technique using a model 1666 slurry packer (Alltech, USA).

Synthesis

Preparation of HP-β-CD bonded stationary phases

The HP-*β*-CD stationary phase was prepared according to the procedures in the previous reports with some modification[17]. Briefly, 6.0 g of HP-*β*-CD was dissolved in 100 mL of dry DMF, to which 1.0 g of sodium hydride was added. The mixture was stirred for 30 min at room temperature. After the unreacted sodium hydride was removed by filtration, 2.0 mL of 3-(triethoxysilyl) propyl isocyanate was added to the filtrate, which was kept stirring at 85–90°C. for 5 h under a dry nitrogen atmosphere. Then the reaction mixture was cooled to room temperature and activated silica gel (5.0 g) was added. The reaction

e-mail: lmd@dns.sxnu.edu.cn

mixture was allowed to react for 24 h at 110–120°C. The obtained solid was filtrated and washed with DMF, doubly distilled water, methanol and acetone in sequence to give HP-*β*-CD bonded stationary phase. The results of elemental analysis (%): C, 8.78; H, 1.69; N, 2.07.

Preparation of HP-β-CD-SWCNTs bonded stationary phases

Acyl chloride-functionalized SWCNTs were prepared as follows[18,19]: 30 mg of the purified SWCNTs were suspended in 80 mL of a 3:1 mixture of concentrated H_2SO_4/HNO_3 in a 250-mL flask and sonicated in a water bath for 4 hours at 35–40ºC. The resultant suspension was then diluted with 400 mL of water and sedimentated for 3 days. The shortened SWCNTs-COOH were collected by centrifugation and washed with water and dried. Forty milligrams of the shortened SWCNTs-COOH were stirred in 10 mL of $SOCl_2$ at 75°C. for 24 hours and the solvent was evaporated.

SWCNTs-COCl (20 mg) reacted with 6.0 g of HP-*β*-CD in 100 mL of dry DMF at 90°C. for 7 days under a pure nitrogen atmosphere. To the solution, 1.0 g of NaH was added and the mixture was stirred for 30 min at room temperature. After filtration to remove unreacted sodium hydride and SWCNTs-COCl, 2.0 mL of 3-(triethoxysilyl) propyl isocyanate was added to the filtrate, which was kept stirring at 85–90°C. for 5 h. Subsequently, activated silica gel (5.0 g) was added to the reaction mixture at room temperature. The mixture was allowed to react for 24 h at 110–120°C. The resulting recipitate was filtrated and washed with DMF, doubly distilled water, methanol and acetone in sequence, yielding 5.5 g of brown solid. The results of elemental analysis (%): C, 6.59; H, 1.41; N 0.61.

The reactions for preparation of the HP-*β*-CD-SWCNTs stationary phase are depicted in Figure 1.

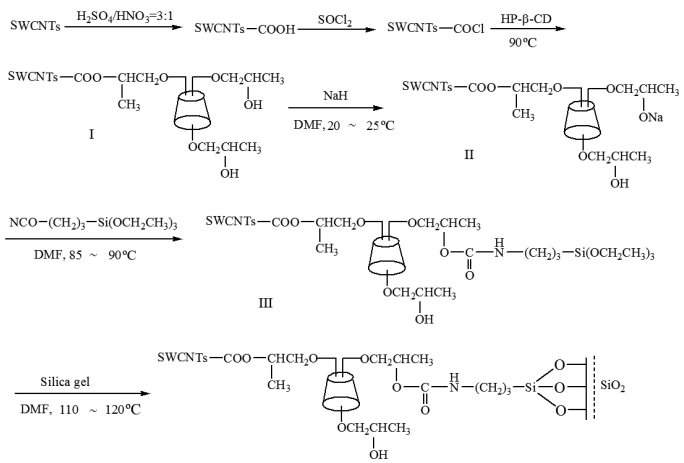

Figure 1. Scheme for preparation of the HP-β-CD-SWCNTs stationary phase.

Experimental methods

The packing materials were dispersed into methanol/chloroform (3:1, *v/v*) and packed into the stainless steel column (250 mm × 4.6 mm i.d.) with methanol used as eluent at 40 MPa by a slurry packing technique. The column was rinsed online with methanol and then equilibrated with methanol/water as the eluent at a flow rate of 1.0 mL.min^{-1} until a stable baseline was obtained. If the mobile phase was changed, the column was washed at least 1 h with the new mobile phase before injecting the sample. Chromatographic separations of the PAHs were performed with water/methanol (5:5, *v/v*) as mobile phase. Nevertheless, the dipine analogues were performed with triethylammonium acetate buffer (0.1%, *v/v*, pH 4.1)/methanol (7:3, *v/v*) as mobile phase. All sample injections were held constant at 10 mL through the use of a fixed-volume injection loop. Throughout this study, the flow rate was 1.0 mL.min^{-1} at 30°C. and all the test samples were detected at 254 nm. Methanol or acetonitrile which was used to dissolve test samples and methanol was also used as the non-retained compound for estimating the dead time (t_0).

RESULTS AND DISCUSSION

Separation of the PAHs and benzene

First, eight PAHs (Figure 2), which were benzene (1), diphenyl (2), naphthalene (3), fluorene (4), acenaphthene (5), phenanthrene (6), benzanthracene (7), and benzopyrene(8), were separated on the HP-*β*-CD and HP-*β*-CD-SWCNTs columns. In an attempt to optimize the separation on the two columns, various mobile phases such as water/methanol, water/acetonitrile, or hexane/2-propanol were tried. The best separation was obtained using water/methanol (5:5, *v/v*) as the mobile phase. Table 1 shows the retention times (t_R) and capacity factors (k') of eight polycyclic aromatic hydrocarbons with water/methanol (5:5, *v/v*) mobile phase on the two stationary phases. Figure 3 exhibits the chromatograms of these analytes on the HP-*β*-CD and HP-*β*-CD-SWCNTs columns.

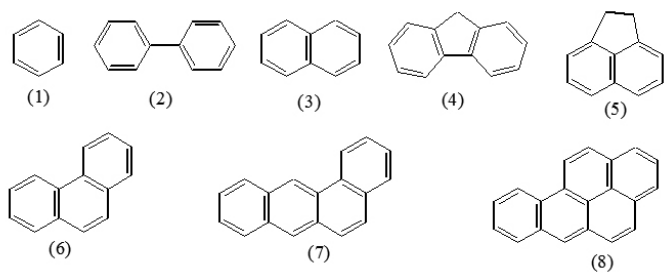

Figure 2. The molecular structure of eight PAHs.

Table 1. The retention times (t_R/min) and capacity factors (*k'*) of the PAHs on the HP-*β*-CD and HP-*β*-CD-SWCNTs columns.

Test solutes		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
HP-*β*-CD	t_R	8.016	40.986	14.793	14.793	11.187	24.439	40.986	40.986
	k'	1.50	11.81	3.62	3.62	2.50	6.64	11.81	11.81
HP-*β*-CD-SWCNTs	t_R	6.106	21.066	9.141	12.903	7.527	13.338	29.408	34.021
	k'	2.90	12.45	4.84	7.24	3.81	7.52	17.78	20.72

As can be seen from Table 1 and Figure 3, diphenyl (2), benzanthracene (7) and benzopyrene(8) could not be separated on the HP-*β*-CD column, naphthalene (3) and fluorene (4) could also not be separated on this column. However, the best separation of all of them could be obtained on the HP-*β*-CD-SWCNTs column. This means that there existed the additional interaction between the solutes and HP-*β*-CD-SWCNTs column. The additional interaction was possibly a π-π interaction between SWCNT and an aromatic group. The more the number of aromatic ring, the stronger π-π interaction is generated. Whereas complete resolution of fluorene (4) and phenanthrene (6) was achieved on the HP-*β*-CD column, only partial separation was achieved on the HP-*β*-CD-SWCNTs column. In short, the separation ability of the HP-*β*-CD-SWCNTs column was better than that of the HP-*β*-CD column for these PAHs. SWCNTs leads to the stronger π-π interactions. The synergism of SWCNTs and HP-*β*-CD makes more effective selectivity for these PAHs.

On the other hand, compared with the SWCNTs bonded silica gel column[16], there were better separation for these aromatic hydrocarbons on the HP-*β*-CD-SWCNTs column. Only several PAHs can be separated with a mobile phase on the SWCNTs bonded silica gel column.

Separation of the similar dipine drugs

In order to further investigate the separation ability of the two columns. Secondly, six structurally similar dipine drugs were separated on the HP-*β*-CD and HP-*β*-CD-SWCNTs columns, which were nimodipine (1), nicardipine (2), nitrendipine (3), amlodipine (4), felodipine (5), and nisodipine (6) (Figure 4). In an attempt to optimize the separation, various mobile phases such as water/methanol, or water/acetonitrile were employed and the peak shape was adjusted with triethylammonium acetate buffer solution. The solvent of (3:7,

v/v) methanol/triethylammonium acetate buffer (0.1%, *v/v*, pH 4.1) as the mobile phase gave the best resolution. The retention times and capacity factors of six dipine drugs with this mobile phase on the HP-*β*-CD and HP-*β*-CD-SWCNTs columns are listed in Table 2.

The chromatograms of six dipine drugs on the HP-*β*-CD and HP-*β*-CD-SWCNTs columns are shown in Figure 5. From Table 2 and Figure 5, it can be seen that six dipine drugs obtained the best separation on the HP-*β*-CD-SWCNTs column. Three solutes of nimodipine (1), nitrendipine (3) and felodipine (5), which all contain two benzene rings, could not be separated on the HP-*β*-CD column, whereas the best separation was achieved on the HP-*β*-CD-SWCNTs column. This means that there existed the hydrophobic interaction with exception of the π-π interaction between the solutes and SWCNTs. SWCNTs can assist HP-*β*-CD with enhancing chromatographic characteristics. The drugs nicardipine (2), amlodipine (4), and nisodipine (6), which were resoluted on the HP-*β*-CD column, were also separated on the HP-*β*-CD-SWCNTs column. Nevertheless, the solute of the longest retention time is nicardipine (2) with three benzene rings. This can be caused by the strong π-π interaction between SWCNTs and aromatic rings. All in all, the separation ability of the HP-*β*-CD-SWCNTs column was better than that of the HP-*β*-CD column for these six dipine drugs.

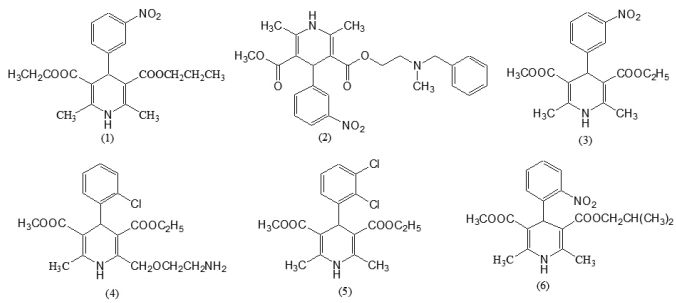

Figure 4. The molecular structure of six dipine drugs

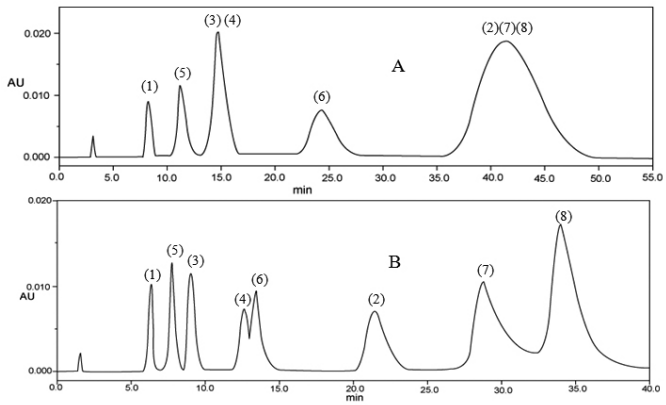

Figure 3. Chromatograms of the PAHs on the two columns
(A) on the HP-β-CD column; (B) on the HP-β-CD-SWCNTs column. HPLC conditions: silica gel, 5 μm particle size; column size, 250 mm × 4.6 mm; mobile phase, water/methanol (5:5, v/v); flow rate, 1.0 mL.min^{-1}; temperature, 30 ºC; UV detection, 254 nm; injection volume, 10 μL; the concentrations of polycyclic aromatic hydrocarbons: (1) benzene (200 μg.mL^{-1}); (2) diphenyl (8 μg.mL^{-1}); (3) naphthalene (35 μg.mL^{-1}); (4) fluorene (8 μg.mL^{-1}); (5) acenaphthene (100 μg.mL^{-1}); (6) phenanthrene (3.5 μg.mL^{-1}); (7) benzanthracene (10 μg.mL^{-1}); (8) benzopyrene (10 μg.mL^{-1}).

Table 2. The retention times (t_R/min) and capacity factors (k') of six dipine drugs on the HP-*β*-CD and HP-*β*-CD-SWCNTs columns

Test solutes		(1)	(2)	(3)	(4)	(5)	(6)
HP-*β*-CD	t_R,	18.032	12.218	18.032	7.670	18.032	25.683
	k',	4.633	2.817	4.633	1.396	4.633	7.023
HP-*β*-*CD*-SWCNTs	t_R,	14.722	46.677	11.150	25.029	17.267	20.627
	k',	3.904	14.549	2.714	7.337	4.752	5.871

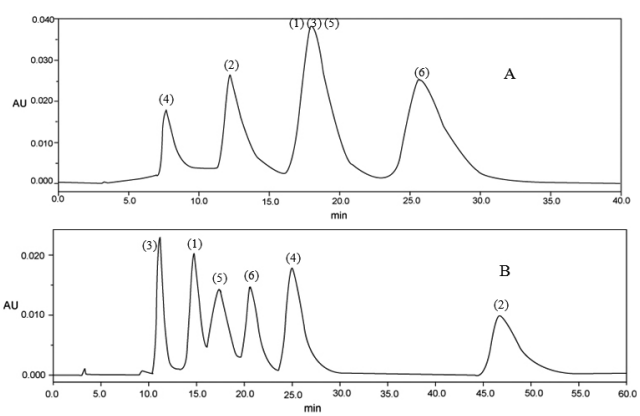

Figure 5. Chromatograms of dipine drugs on the two columns
(A) on the HP-*β*-CD column; (B) on the HP-*β*-CD-SWCNTs column. HPLC conditions: silica gel, 5 μm particle size; column size, 250 mm × 4.6 mm; mobile phase, triethylammonium acetate buffer (0.1%, *v/v*, pH 4.1)/methanol (7:3, *v/v*); flow rate, 1.0 mL.min^{-1}; temperature, 30 ºC; UV detection, 254 nm; injection volume, 10 μL; the concentrations of dipine drugs: (1) nimodipine (8 μg.mL^{-1}); (2) nicardipine (8 μg.mL^{-1}); (3) nitrendipine (8 μg.mL^{-1}); (4) amlodipine (15 μg.mL^{-1}); (5) felodipine (8 μg.mL^{-1}); (6) nisodipine (8 μg.mL^{-1}).

Determination of the PAHs in the coke wastewater on the HP-*β*-CD-SWCNTs column

The linearities of the PAHs in standard solutions were investigated at nine concentration levels. Standard working solutions of appropriate concentrations were prepared by dilution of stock standard solutions with acetonitrile before use. Based upon the corresponding chromatography conditions described above, triplicate 10 μL injections were made three times for each concentration and chromatographed on the HP-*β*-*CD*-SWCNTs column. The peak areas were plotted against the corresponding concentrations to obtain the calibration graphs. the linear ranges and regression equations of the PAHs are listed in Table 3. The correlation coefficients ranged from 0.9991 to 0.9995, indicating good linearity. The small value of variance confirmed the small degree of scattering of the experimental data points around the regression line.

Table 3. The linear ranges and regression equations of PAHs.

PAHs	linear ranges/ (μg mL^{-1})	regression equations*	R^2
benzene (1)	0.1–300	Y=1912X+4510	0.9994
diphenyl (2)	0.01–50	Y=113262X+32451	0.9992
naphthalene (3)	0.02–100	Y=14815X+43022	0.9995
fluorene (4)	0.01–20	Y=77114X–131943	0.9991
acenaphthene (5)	0.05–200	Y=4126X+18402	0.9994
phenanthrene (6)	0.01–20	Y=139125X+89066	0.9992
benzanthracene (7)	0.04–30	Y=133967X+80035	0.9991
benzopyrene(8)	0.01–30	Y=260244X+45885	0.9991

*X/the concentrations of PAHs (mg mL^{-1}), Y/the peak areas (mV.s); injection volume, 10 mL

The HP-*β*-*CD*-SWCNTs column was applied in the determination of the seven PAHs in the coke wastewater. The coke wastewater samples were analysed as described in Nation Environmental Protection Standards HJ 478-2009 method using 30 mL of n-hexane to extract 1 L of coke wastewater, repeating two times. The extract was then concentrated to 0.5 mL in a concentrated bottle at 40ºC with a nitrogen flow. The residues were then fixed to 1 mL in ethanol. The solution was filtered through a 0.45 μm organic millipore membrane filter. An aliquot was injected into the chromatographic system. The experiment determined that the concentrations of (2)–(8) PAHs were 0.06 mg.L^{-1}, 1.2 mg.L^{-1}, 0.04 mg.L^{-1}, 4.3 mg.L^{-1}, 0.02 mg.L^{-1}, 0.0 mg.L^{-1}, 0.03 mg.L^{-1}, respectively. Benzanthracene (7) was not detected in the coke wastewater sample. Figure 6 exhibits the chromatograms of the coke wastewater sample.

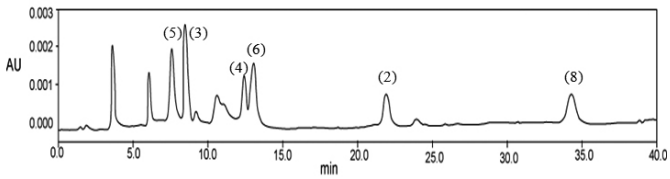

Figure 6. Chromatograms of the coke wastewater sample.

In order to verify the precision and accuracy for the measure. The coke wastewater sample spiked with seven PAHs at each 1 mg.L^{-1} was used for recovery assay, repeating two times. The preparation process was the same as above. The recovery values of (2)–(8) PAHs were 65.7%, 63.6%, 75.2%, 69.8%, 76.4%, 103.3%, and 105.1%, respectively. The relative standard deviation (RSD) values were within 0.67%–1.58%. The results are in general agreement with that of Nation Environmental Protection Standards HJ 478-2009 method.

Duration of the stationary phase

The elemental analysis results of the HP-*β*-*CD*-SWCNTs chromatographic packings that were steeped for 48 hours within pH 2~8 at 50ºC were hardly changed, which indicated that the stationary phase will not be hydrolyzed in the range of pH 2 to 8. In addition, the HP-*β*-*CD*-SWCNTs chromatographic parameters such as column pressure, column efficiency, and retention time of sample were also not variable after the column was injected 300 needles. Chromatographic performance of the column was remained unchanged after the chromatographic column was placed for 3 months. In all, the stability of the HP-*β*-*CD*-SWCNTs column was good.

CONCLUSIONS

The π-π interaction and the hydrophobic interaction in the stationary phase is improved by introducing the SWCNTs to HP-*β*-CD, which can assist HP-*β*-CD with enhancing chromatographic characteristics. The HP-*β*-CD-SWCNTs column possess a good selectivity toward the investigated PAHs and analogues. These materials achieved better separation on the HP-*β*-CD-SWCNTs column than on the HP-*β*-CD column. The HP-*β*-CD-SWCNTs column had also stronger separation ability for these aromatic hydrocarbons compared to the column of the SWCNTs bonded silica gel column. The SWCNTs make it possible to extend the application range on the newly prepared stationary phases for HPLC.

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