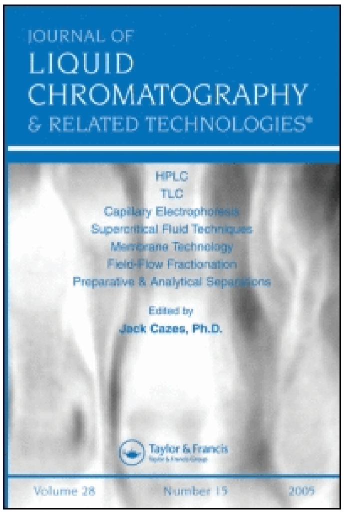

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Single-Wall Carbon Nanotubes Used as Stationary Phase in HPLC

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Abstract: The single wall carbon nanotubes (SWNTs) were first bonded to 3-aminopropyl silica gel and used as a stationary phase in high performance liquid chromatography. With different mobile phases, seven polycyclic aromatic hydrocarbons were separated. The results showed that SWNTs had a stronger interaction between the aromatic group and SWNTs. This work indicated that SWNTs make it possible to extend the application range on the newly prepared chromatographic stationary phases for HPLC.

Keywords: Single-wall carbon nanotubes, Stationary phase, Polycyclic aromatic hydrocarbon, HPLC

INTRODUCTION

Carbon nanotubes (CNT) have been widely recognized as quintessential nanomaterials having high strength, surface area, adsorption ability, and nanoscale interactions. CNT exists as single walled nanotubes (SWNTs) or multiple walled nanotubes (MWNTs), and also as open or close ended structures of different morphology and diameter. SWNT consists of a grapheme sheet rolled into a cylinder with a typical diameter on the order of 1 nm. MWNT consists of concentric cylinders with an interlayer spacing of 0.34 nm and a diameter typically on the order of 10–20 nm.[1] With novel structural, electronic, and mechanical properties, SWNTs constitute an important new form of carbon that may find applications in many fields. The

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functionalization chemistry of the open ends, the exterior cavity (concave face) of the SWNTs, is expected to play a vital role in tailoring the properties of these materials and the engineering of nanotube devices.[2] Since their discovery in 1991, they have stimulated intensive research into potential high impact applications such as nanoelectronic devices, catalyst supports, biosensors, filler based application, and hydrogen storage.[3]

Different types of chromatography were used to remove nanoparticles from CNT samples and to separate functionalized CNT by length. In order to determine environmental water samples, multi-walled carbon nanotubes were used as a solid phase extraction adsorbent.[4] Self-assembled CNTs were used in long capillary tubes for the development of gas chromatography columns,[5] and electrochemical detectors with CNT modified electrodes were used in liquid chromatography and capillary electrophoresis, achieving significantly lower operating potentials and yielding substantially enhanced signal-to-noise characteristics. 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.[6]

Recently, our research group has bonded SWNTs to the fused silica capillary tubing and reported that the SWNTs assist ionic liquid with enhanced chromatographic characteristics in GC.[7] Here, we first synthesized single-wall carbon nanotubes bonded 3-aminopropyl silica gel, which were used as stationary phase to separate polycyclic aromatic hydrocarbon with different mobile phases in HPLC. We found that this stationary phase had stronger separation ability for polycyclic aromatic hydrocarbons compared to the stationary phase of 3-aminopropyl silica gel.

EXPERIMENTAL

Materials

Single-walled carbon nanotubes, (3-aminopropyl)-triethoxysilane, and polycyclic aromatic hydrocarbons were purchased from Aldrich or Fluka. Silica gel (YWG-80, particle size 5 μm, pore size 7 nm), was obtained from Qingdao Ocean Chemical Factory (China). All other reagents were of analytical reagent grade from Shanghai Chemical Factory (China). Solvents used in chromatographic experiments were of HPLC grade.

Apparatus

The HPLC experiments were performed with a Shimadzu LC-6A pump, a spectra-SPD-10AVP UV detector, and a CR-5A integrator (Shimadzu, Kyoto, Japan). The 250 mm × 2 mm HPLC empty columns and an air driven fluid pump were from Alltech (USA).

Preparation of Stationary Phases

Acyl chloride SWNTs were prepared as follows.[2,8]: 50 mg of the purified SWNTs were suspended in 200 mL of a 3:1 mixture of concentrated H_2SO_4/HNO_3 in a 500 mL flask and sonicated in a water bath for 6 hours at 35°C to 40°C. The resultant suspension was then diluted with 1000 mL of water, and sedimented for 3 days. The shortened SWNTs were collected by centrifugation and washed with 100 mL water and dried. The shortened SWNTs (50 mg) were stirred in 5 mL of $SOCl_2$ at 75°C for 24 hours and the solvent was evaporated. The residue was dispersed in 20 mL of dry dimethylformamide (DMF).

The silica gel was silanized using (3-aminopropyl)-triethoxysilane in benzene at 80°C before use.[9] 3-aminopropyl-silica gel (1.2 g) and 20 mL of DMF containing 50 mg of SWNT-COCl were added into a 50 mL flask to react for 72 hours at 85°C in the presence of N_2. Then the cooled solution was filtered and washed carefully with DMF, methanol, and dried under vacuum. Finally, 1.1 g of brown solid was obtained.

HPLC Procedure

The above single-wall carbon nanotubes stationary phases were slurry packed into 250 mm × 2.0 mm HPLC columns at 40 MPa using an air driven fluid pump and hexane/2-propanol (9 : 1, v/v) as the slurry solvent. The column was rinsed online with ethanol for 3 hours and then equilibrated with hexane-2-propanol (9 : 1, v/v) as the eluent at a flow rate of $0.2\ \mathrm{mL} \cdot \mathrm{min}^{-1}$ until a stable baseline was reached. If the mobile phase was changed, the column was washed at least 2 hours with the new mobile phase before injecting the sample. The same packing method was also used for preparation of the 3-aminopropyl silica gel column.

Throughout this study, chromatographic separations were performed at 30°C and all the test solutes were detected at 254 nm. The mobile phases were filtered and sonicated prior to use.

RESULTS AND DISCUSSION

First, seven polycyclic aromatic hydrocarbons (benzene (1), diphenyl (2), naphthalene (3), fluorene (4), anthracene (5), phenanthrene (6), benzanthracene (7)) were separated on single-wall carbon nanotube columns using

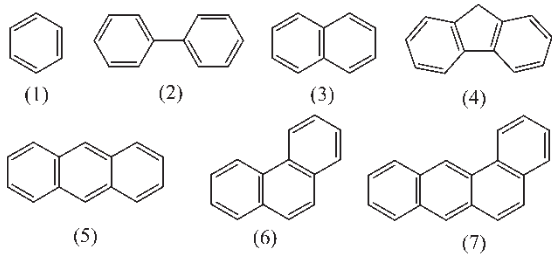

Figure 1. The molecular structure of seven polycyclic aromatic hydrocarbons.

hexane/2-propanol (7:3, v/v) as the mobile phase (Fig. 1). Table 1 shows that their retention times were changed at different flow rates of 0.1, 0.2, and 0.3 mL · min^{-1}, respectively. When the flow rate of mobile phase was 0.2 mL · min^{-1}, it provided reasonably retention time and resolution. Therefore, the flow rate of 0.2 mL · min^{-1} was used in all experiments.

Seven polycyclic aromatic hydrocarbons were also separated on a 3-aminopropyl silica gel column using hexane/2-propanol (7:3, v/v) as the eluent at a flow rate of 0.2 mL · min^{-1}. Their retention times were about 5.1 min and no separations were observed. This showed that the single-wall carbon nanotubes for polycyclic aromatic hydrocarbons possessed relatively high recognition ability compared to the 3-aminopropyl silica gel column.

In an attempt to optimize the separation on the single-wall carbon nanotubes column, various mobile phases were employed. With the hexane/2-propanol (9:1, v/v) as the mobile phase, the separations took a longer time. The reverse-phase separation of polycyclic aromatic hydrocarbons was carried out by using acetonitrile/water (6:4, v/v) as the eluent, it gave a different eluting order. Polycyclic aromatic hydrocarbons were also separated by using methanol as the eluent. Their retention times are listed in Table 2.

Figure 2 exhibits the chromatograms of polycyclic aromatic hydrocarbons in hexane/2-propanol (7:3, v/v), acetonitrile/water (6:4, v/v), and

Table 1. The retention times (min) of polycyclic aromatic hydrocarbon at different flow rates

Flow rate (mL · min^{-1}) (hexane/2-propanol (7:3, v/v))	Test solutes						
	1	2	3	4	5	6	7
0.1	9.736	14.388	14.388	23.473	65.321	65.321	23.473
0.2	4.883	5.892	5.892	9.375	48.361	48.361	9.375
0.3	3.275	3.983	3.983	6.683	36.517	36.517	6.683

Table 2. The retention time (min) of polycyclic aromatic hydrocarbon with different mobile phase

Mobile phase	1	2	3	4	5	6	7
Hexane/2-propanol (9:1, v/v)	7.992	13.365	13.365	18.382	61.766	61.766	18.382
Hexane/2-propanol (7:3, v/v)	4.883	5.892	5.892	9.375	48.361	48.361	9.375
Acetonitrile/water (6:4, v/v)	6.108	11.833	10.222	20.617	67.175	67.175	6.108
Methanol	5.066	7.669	7.669	15.178	46.433	46.433	5.066

methanol mobile phase at a flow rate of 0.2 mL · min^{-1}. The solvent of acetonitrile/water (6:4, v/v) gave the best resolution.

The possible mechanism for the single-wall carbon nanotubes to recognize polycyclic aromatic hydrocarbons is that a nonpolar interaction, such as a π-π interaction between CNT and an aromatic group, may play some role in separation.

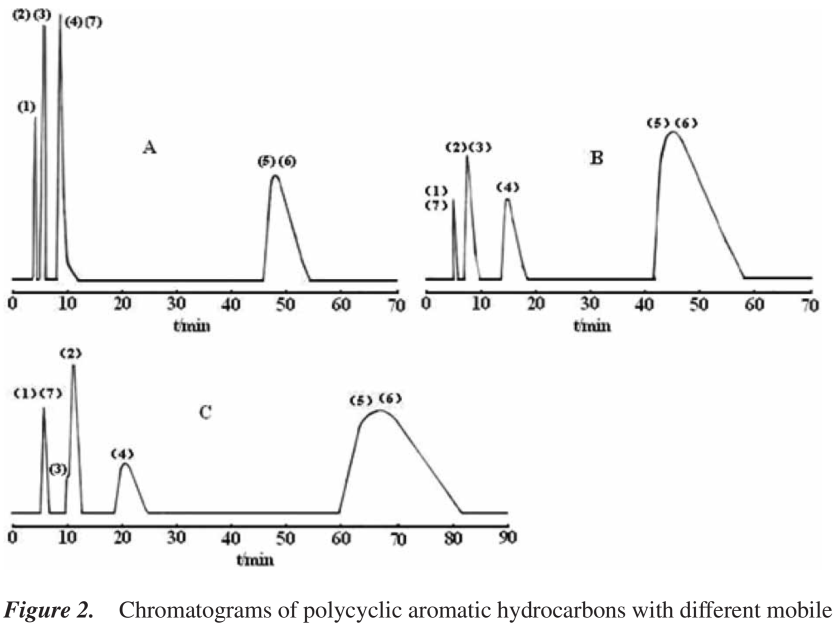

Figure 2. Chromatograms of polycyclic aromatic hydrocarbons with different mobile phases. A: hexane/2-propanol (7:3, v/v); B: methanol; C: acetonitrile/water (6:4, v/v). HPLC conditions: column size, 250 mm × 2.0 mm; flow rate, 0.2 mL · min^{-1}; temperature, 30°C; detection, 254 nm.

CONCLUSION

From the above comprehensive study, we know that when the SWNTs were used as stationary phase in HPLC, it had good separation ability for polycyclic aromatic hydrocarbons. The SWNTs make it possible to extend the application range on the newly prepared chromatographic stationary phases for HPLC.

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