Short communication

Evaluation of multi-walled carbon nanotubes as gas chromatographic column packing

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Abstract

Purified multi-walled carbon nanotubes (PMWCNTs), activated charcoal and graphitized carbon black (Carbopack B) were used as column packing materials to compare their separation ability and other gas chromatographic behavior for aromatic hydrocarbons, alkanes, halogenated hydrocarbons, alcohols, ketones, esters, and ethers. The results show that PMWCNTs can be an excellent gas chromatographic packing material. Compared to Carbopack B with the same surface area, PMWCNTs had a stronger retention ability, a more homogenous surface and smaller theoretical plate numbers. Polar compounds can present symmetric peaks on PMWCNTs. PMWCNTs were found to be an interesting alternative adsorbent to activated charcoal and Carbopack B as gas chromatographic column packing material for volatile compounds, especially those with relatively low boiling points.
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1. Introduction

Carbon sorbents have long been used as adsorbents for the adsorption and separation of volatile organic compounds [1–3]. In recent years, there has been much research focussing on the study of the properties and applications of different types of carbon sorbents. The characteristics of new types of activated charcoal and graphitized carbon black have been investigated, and their utilization for the analysis of volatile organic compounds has been exploited [4–10]. The surface chemistry of carbons is de-

termined to a large extent by the number and the nature of the surface functional groups or complexes. It is suggested that oxygen is present on the carbon surface as organic functional groups [11]. The number of oxygen-containing surface functional groups can vary over a wide range, as can their reactivity, and both depend on the type of oxidizing agent used and the conditions during the modification process. Oxidation of carbons with hot air results in a greater proportion of relatively weak acidic surface functional groups (i.e., phenolic), whereas nitric acid modification produces a greater amount of carboxylic groups [9].

Since their first observation a decade ago [12], carbon nanotubes have been the focus of considerable research. From their unique electronic properties

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and a thermal conductivity higher than diamond, to mechanical properties where the stiffness, strength and resilience exceed any current material, carbon nanotubes offer tremendous opportunities for the development of new material systems [13]. Due to their curved internal surface, nanotubes show a stronger binding ability for molecules compared to a planar carbon surface. Carbon nanotubes are now being investigated as the fundamental molecular units for nanoelectronic devices, catalyst supports, and sorbents for drug delivery. Access into the internal surface of the nanotubes is required for most of these applications. Many investigators have reported remarkable physical and mechanical properties for this new form of carbon.

Carbon nanotubes can be single-walled or multi-walled structures. In multi-walled carbon nanotubes (MWCNTs), several layers of graphitized carbon and a hollow core are evident. The surface [14] and electrochemical properties [15], electronic conduction [16], as well as nitrogen adsorption and capillarity [17] of MWCNTs have been investigated.

The goal of this study was to investigate the gas chromatographic properties of MWCNTs and to determine the possibility of using MWCNTs as gas chromatographic column packing material. In the study, MWCNTs were purified to reduce the number of polar groups on the surface, remove the catalyst residuals and open the ends of the carbon nanotubes. The chromatographic properties of the purified MWCNTs (PMWCNTs), activated charcoal and graphitized carbon black with respect to groups of selected compounds were investigated and compared.

2. Experimental

2.1. Materials

Seven groups of compounds were chosen as the tested chemicals, namely aromatic hydrocarbons, alkanes, halogenated alkanes, alcohols, ketones, esters, and diethyl ether. Benzene, toluene, *p*-xylene, *m*-xylene, *o*-xylene, ethyl benzene, *n*-pentane, *n*-hexane, cyclohexane, *n*-heptane, dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, methanol, ethanol, acetone, 2-butanone, diethyl ether, methyl acetate, and ethyl acetate, all

analytical grade, were purchased from Shanghai Chemical (Shanghai, China). 2-Propanol, *n*-propanol, *sec*-butanol, and *n*-butanol, all chromatography grade, were purchased from Beijing Chemical (Beijing, China).

Activated charcoal (60–80 mesh, surface area 600 m^2/g) was of chromatography grade from Shanghai Charcoal Factory (Shanghai, China). Carbopack B (60–80 mesh, surface area 100 m^2/g) was purchased from Supelco (Bellefonte, PA, USA)

MWCNTs were kindly provided by the Department of Chemistry, Xiamen University. They were prepared by the Ni–MgO catalytic decomposition of methane [18] and washed with 6 mol/dm^3 HNO$_3$, with an O.D. of 15–30 nm and an I.D. of 3 nm. Their X-ray diffraction (XRD) patterns are very similar to that of graphite, but the XRD features are somewhat broadened, indicating that the degree of long-range order of these nanostructures is relatively low in comparison with that of graphite [19]. The MWCNTs were ground and sieved, the particles between 60 and 80 mesh with a surface area of 98 m^2/g were selected and further treated with H$_2$ at 10 cm^3/min at 900 °C for 24 h, refluxed with 6 mol/dm^3 hydrochloric acid for 24 h, and then washed with distilled water to clean up the catalyst residual, limit the hydrophilic functional groups on the surface and open the ends of the tubes. The purified MWCNTs (PMWCNTs) were used in the study.

The gas standards were prepared by injecting liquid chemicals of the same group into a 100 cm^3 vial sealed with a silicon rubber cap. The liquid volume was between 0.1 and 1.0 mm^3, depending on the volatility and molecular mass of the compound. The head-space gas was taken as the gas standard and 100 mm^3 was injected into the gas chromatograph with a syringe. Due to the very high retention, only head-space gases of single benzene, *n*-pentane, dichloromethane and ethanol were analyzed on the column packed with activated charcoal.

2.2. Gas chromatography

PMWCNTs (1.5 g), 1.6 g activated charcoal, and 1.0 g Carbopack B were packed into a glass chromatographic column of 50 cm length and 0.3 cm I.D. The packing length was 30 cm. The columns were

conditioned at 320 °C with a N$_2$ gas flow of 20 cm^3/min for 5 h.

Samples were analyzed with a Shimadzu GC-9A gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector. The injection port and detector temperatures were both set at 250 °C. The oven temperature was set differently depending on the chemical group tested and on the column packing.

The gas flow was 60 cm^3/min for N$_2$ carrier gas, 45 cm^3/min for H$_2$, and 300 cm^3/min for air. Samples and standards were run in triplicate. Chromatograms were recorded by HW chromatographic data processing software (Qianpu Software, Nianjing, China).

3. Results and discussion

3.1. Comparison of chromatographic behavior with respect to aromatic hydrocarbons

Three columns packed with activated charcoal, Carbopack B, and PMWCNTs, respectively, were used as the chromatographic columns for the separation of aromatic hydrocarbons. Only benzene was loaded on the activated charcoal column, and a symmetric peak was observed at 6.46 min at 320 °C. The retention time was so long that no other aromatic hydrocarbon was tested on the activated charcoal column. The separation of benzene, toluene, *p*-xylene, *m*-xylene, *o*-xylene and ethyl benzene on the Carbopack B and PMWCNTs columns is illustrated in Fig. 1. In the chromatograms, *p*-xylene and ethylbenzene co-eluted, and *m*-xylene and *o*-xylene were partially separated on both columns. All the peaks were almost symmetric. Peaks on PMWCNTs had slightly less resolution. It was observed that to elute the same tested compounds from the PMWCNT column, a much higher desorption temperature was required than for the Carbopack B column.

3.2. Comparison of chromatographic behavior with respect to alkanes

Again, the three columns packed with different packings were compared. *n*-Pentane, *n*-hexane, cyclohexane, and *n*-heptane were selected as repre-
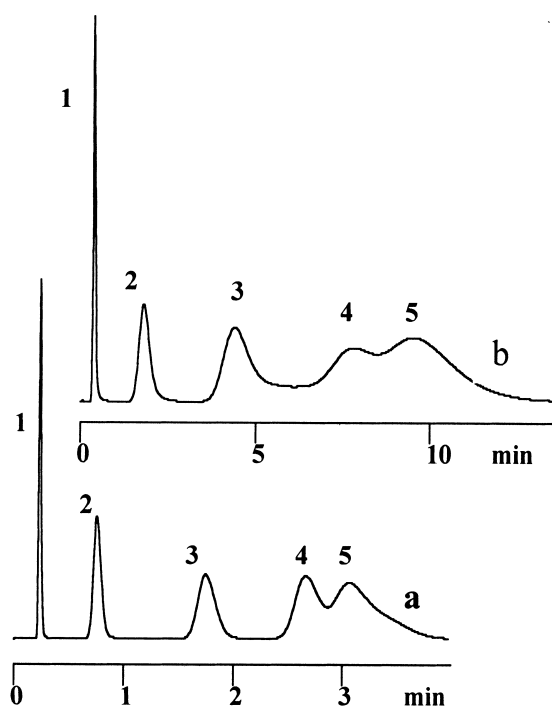

Fig. 1. Chromatograms of aromatic hydrocarbons on the Carbopack B and PMWCNTs columns. (a) Carbopack B column, oven temperature 260 °C. (b) PMWCNT column, oven temperature 320 °C. Peaks: 1=benzene, 2=toluene, 3=*p*-xylene/ethylbenzene, 4=*m*-xylene, 5=*o*-xylene.

sentative compounds of the alkane group. Because of the strong affinity of activated charcoal for these compounds, only *n*-pentane was injected into the activated charcoal column, which gave a symmetric peak at a retention time of 5.83 min at 280 °C. Fig. 2 shows the separation of the group of compounds on the Carbopack B and PMWCNT columns. A better resolution was observed on the Carbopack B column, which separated *n*-pentane and cyclohexane at baseline. The higher temperature needed for the PMWCNT column reveals the stronger affinity of PMWCNTs.

3.3. Comparison of chromatographic behavior with respect to halogenated hydrocarbons

Four chlorinated hydrocarbons, dichloromethane, trichloromethane, tetrachloromethane and 1,2-dichloroethane, were selected as test compounds for the three columns. Only one compound, dichloromethane, was run on the activated charcoal column, and
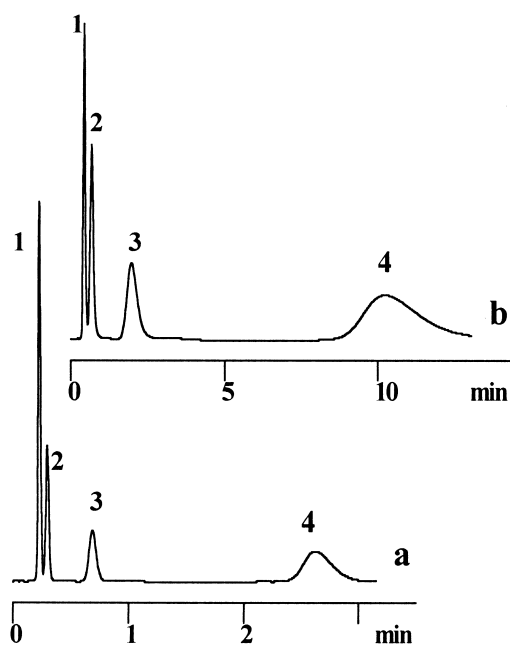
Fig. 2. Chromatograms of alkanes on Carbopack B and PMWCNT columns. (a) Carbopack B column, oven temperature 220 °C. (b) PMWCNT column, oven temperature 280 °C. Peaks: 1=*n*-pentane, 2=cyclohexane, 3=*n*-hexane, 4=*n*-heptane.
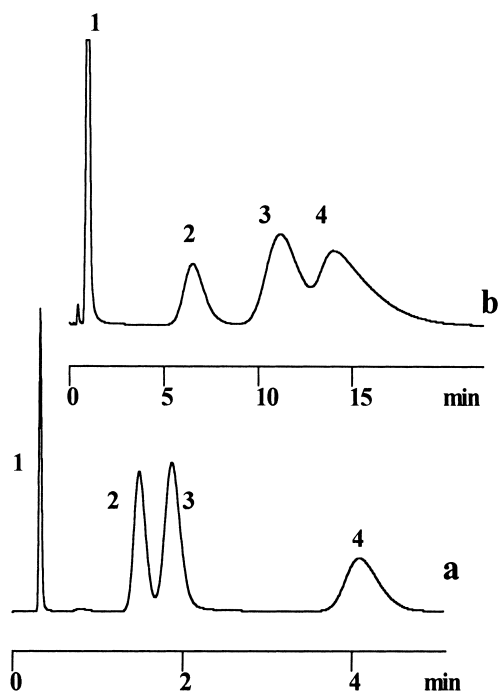

Fig. 3. Chromatograms of halogenated hydrocarbons on the Carbopack B and PMWCNT columns. (a) Carbopack B column, oven temperature 120 °C. (b) PMWCNT column, oven temperature 160 °C. Peaks: 1=dichloromethane, 2=trichloromethane, 3=1,2-dichloroethane, 4=tetrachloromethane.

an asymmetric peak at 28.1 min was found at 160 °C. Fig. 3 shows the chromatograms recorded from the Carbopack B and PMWCNT columns. The best resolution was observed on the Carbopack B column, with four separated peaks. Trichloromethane and tetrachloromethane were baseline separated with a resolution of 1.3 on the Carbopack B column. Unexpectedly, on the PMWCNT column, even though trichloromethane and 1,2-dichloroethane were well separated, the peak of 1,2-dichloroethane shifted so much that it coeluted with tetrachloromethane. This may indicate that it is possible to apply PMWCNTs when special selectivity is required.

3.4. Comparison of chromatographic behavior with respect to alcohols, ketones, esters and diethyl ether

Three different packed columns, activated charcoal, Carbopack B and PMWCNTs, were used for the separation of methanol, ethanol, 2-propanol, *n*-propanol, *sec*-butanol and *n*-butanol. A serious tailing peak was observed on the activated charcoal column for ethanol at 200 °C, and no data were recorded. Interesting results were obtained for the other two columns, as shown in Fig. 4. Carbopack B clearly exhibits less separation efficiency for alcohols than PMWCNTs. It should be noted that the peaks were asymmetric and tailing, showing some irreversible interactions between the packing material and alcohols, probably due to the heterogeneous surface and residual hydrophilic groups. It was found that Carbopack B is not an ideal material for the separation of alcohols. On the other hand, PMWCNTs produced a better chromatogram with respect to peak shape and resolution for the six alcohols tested. The peaks for 2-propanol and *n*-propanol slightly overlapped, while the other peaks were well separated. This shows that the number of hydrophilic groups on the PMWCNT packing surface is small and it has a better surface homogeneity.
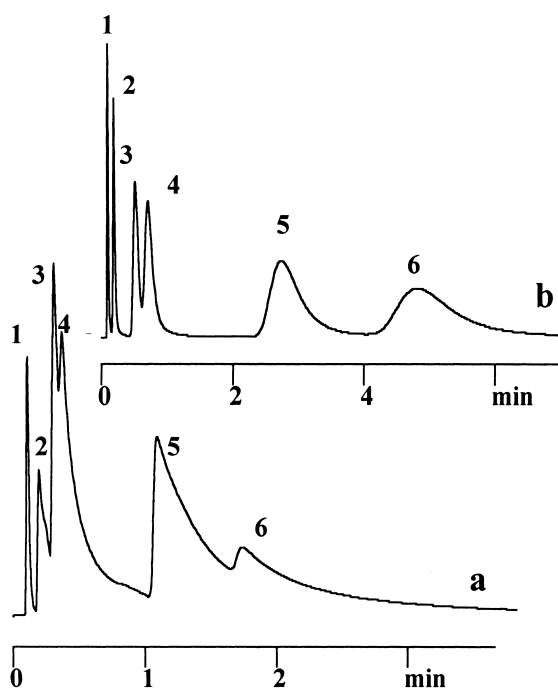
Fig. 4. Chromatograms of alcohols on the Carbopack B and PMWCNT columns. (a) Carbopack B column, temperature 140 °C. (b) PMWCNT column, oven temperature 200 °C. Peaks: 1=methanol, 2=ethanol, 3=2-propanol, 4=*n*-propanol, 5=*iso*-butanol, 6=*n*-butanol.

Typical ketones, esters and diethyl ether were selected to examine the chromatographic behavior of Carbopack B and PMWCNTs. Typical chromatograms are shown in Fig. 5. Acetone, methyl acetate, diethyl ether, 2-butanone, and ethyl acetate presented asymmetric peaks on the Carbopack B column, and symmetric peaks on PMWCNTs.

3.5. Comprehensive comparison

The surface oxygen complexes and trace metal impurities in the sorbent may influence the surface properties and, consequently, the retention behavior [1,7]. As shown in the chromatograms of Figs. 1–5, more hydrophilic compounds exhibit worse chromatographic behavior on Carbopack B due to the stronger interaction between the polar groups on the surface of the packing material and the hydrophilic compounds. On the other hand, the smaller number of polar groups and the higher surface homogeneity
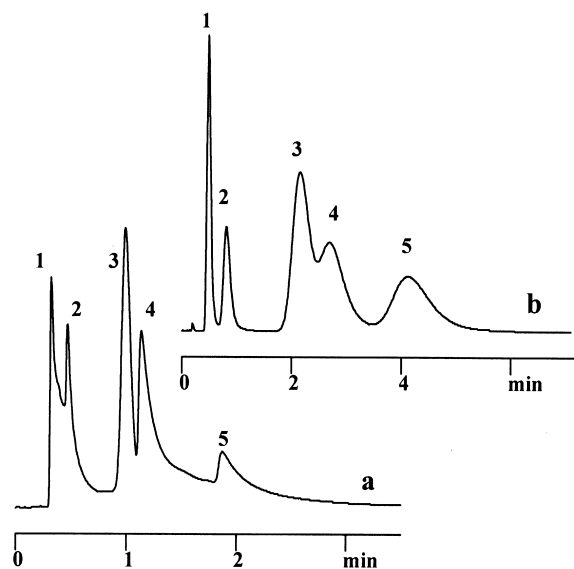

Fig. 5. Chromatograms of ketones, diethyl ether, and esters on the Carbopack B and PMWCNT columns. (a) Carbopack B column, oven temperature 140 °C. (b) PMWCNT column, oven temperature 200 °C. Peaks: 1=acetone, 2=methyl acetate, 3=diethyl ether, 4=2-butanone, 5=ethyl acetate.

of PMWCNTs resulted in faster adsorption kinetics with respect to hydrophilic compounds, showing symmetric chromatographic peaks.

Activated charcoal exhibited the strongest absorption of the materials investigated in this study. At the same column temperature, benzene, *n*-pentane and dichloromethane had much longer retention times on the activated charcoal column than on PMWCNTs. As illustrated in Figs. 1–5, compared to the Carbopack B column, PMWCNTs have a higher absorption, showing a longer retention time for the same compound even with column temperatures 40–60 °C higher. It should be pointed out that the PMWCNTs and Carbopack B used in the study had the same surface areas. Two factors coming together resulted in the greater retention on PMWCNTs. The first was that the amount of PMWCNTs in the column was 1.5-fold that of Carbopack B. However, this was not the main reason for the greater retention on PMWCNTs. Even for columns packed with the same amount of Carbopack B and PMWCNTs, the compounds still showed longer retention times on the PMWCNT column. The second factor was the special property of carbon nanotubes. Carbopack B

Table 1
Theoretical plate numbers and capacity factors for benzene, dichloromethane, and *n*-hexane on three packed columns

Column packing	Benzene		Dichloromethane		*n*-Hexane	
	Plate number/m	k'	Plate number/m	k'	Plate number/m	k'
Activated charcoal	377	106.7	460	467.3	–	–
Carbopack B	1497	2.7	1683	5.4	1727	11.5
PMWCNTs	490	5.5	530	15.1	480	27.9

is a nonporous structure with a planar graphite surface, while PMWCNTs are open-ended, with adsorption sites on both internal and external surfaces. The internal surfaces of open-ended carbon nanotubes exhibit a stronger binding energy and adsorption affinity for compounds [20,21] compared to a planar carbon surface. The second factor could be the main reason for the greater retention on PMWCNTs.

From Figs. 4 and 5 it can be seen that more hydrophilic compounds can be better separated on the PMWCNT column, with symmetric peaks and good resolution. This indicates that PMWCNTs have fewer hydrophilic groups and greater surface homogeneity. The PMWCNT column can be used directly for the separation of some polar compounds without further modification.

Table 1 lists the theoretical plate numbers of typical tested compounds. It was observed that the theoretical plate numbers of the compounds obtained on PMWCNTs were about the same as those on activated charcoal, while Carbopack B had higher plate numbers. The reason for this may be the cavities in both PMWCNTs and activated charcoal, which slow the diffusion of the compounds and therefore reduce the theoretical plate numbers.

4. Conclusion

As shown by the above experiments, PMWCNTs are an interesting alternative adsorbent to activated charcoal and graphitized carbon black as column packing material in gas chromatography or an adsorbent in environmental sampling for volatile compounds. Compared to Carbopack B with the same surface area, PMWCNTs showed the following characteristics: (1) stronger retention of compounds, being suitable for the separation of compounds with relatively low boiling points and both hydrophobic and hydrophilic groups; (2) a more even surface and, therefore, more symmetric peaks; and (3) smaller theoretical plate numbers.

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