



Performance of graphene sheets as stationary phase for capillary gas chromatographic separations



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ABSTRACT

This work presents the investigation of graphene as a new type of stationary phase for capillary GC separations. Graphene capillary column (0.25 mm, i.d.) achieved column efficiency of 3100 plates/m determined by *n*-dodecane at 120 °C. The obtained McReynolds constants suggested the weakly polar nature of graphene sheets as GC stationary phase. As evidenced, graphene stationary phase differs from the conventional phase (5% phenyl polysiloxane) in its resolving ability and retention behaviors, and achieved better separation for the Grob and other mixtures. The advantages of graphene stationary phase may mainly originate from its specific π - π stacking interaction as well as H-bonding interaction. Furthermore, graphene column exhibited good repeatability with relative standard deviation (RSD%) in the range of 0.01–0.07% for run-to-run and 2.5–6.7% for column-to-column, respectively.

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1. Introduction

Graphene with a large delocalized π -electron system and basal shape exhibits fascinating features such as high electrical conductivity, large surface area, good chemical, thermal and mechanical stability [1,2] and has drawn tremendous attention in diverse areas over the past decade [3–7]. The increasing advancements related with graphene are also attributed to its availability via the reduction of graphene oxide (GO) prepared from natural graphite powder according to a modified Hummers' method [8–11]. The reduction can be performed through hydrothermal reduction [12,13], chemical reduction [14] and so forth. Recently, graphene has been reported in separation science as adsorption material for sample preparation [15–24] and as stationary phase for liquid chromatography (LC) [25,26] and capillary electrochromatography (CEC) [25,27].

Research in separation science has shown the high affinity of graphene as sorbent material for aromatic analytes such as substituted phenols [16,19,21], polycyclic aromatic hydrocarbons (PAHs) [17,18,21,22,24], phthalate acid esters (PAEs) [18,20,21] and polyhalogenated biphenyls [18,23] from a sample while leaving possible interferences behind in the sample matrix, which greatly favor the highly selective extraction of aromatic analytes of

interest. However, the high affinity of graphene as stationary phase for aromatics seems not quite favorable for its chromatographic separation of the analytes. As reported, graphene as stationary phase in LC and CEC exhibited severe peak tailings and poor resolution for some aromatics such as naphthalene, biphenyls, alkyl benzenes, PAEs and nitroanilines [25–27].

Considering its superior properties and high chemical and thermal stability, graphene may serve as a good candidate as stationary phase in capillary gas chromatography (GC). Expectedly, graphene may exhibit different separation performance from the currently available GC stationary phases due to its unique structure. As a result of recent survey in the literature, no publications on using graphene as GC stationary phase are available till now. Only one report using GO as GC stationary phase is available [28], in which GO capillary column was used for GC separations below 90 °C possibly due to its poor thermal stability [29]. By contrast, graphene possesses high thermal stability and shows advantages over GO at least in this regard.

Herein, we present the investigation of graphene sheets as GC stationary phase for capillary GC separations. After statically coated onto a fused-silica capillary column, graphene stationary phase was evaluated for separation performance by GC separations of the Grob and other mixtures consisting of different types of analytes, including alkanes, esters, alcohols, amines and benzene derivatives. Meanwhile, a commercial HP-5MS column was also employed for comparison. Additionally, separation repeatability and thermal stability of the columns were examined.

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2. Experimental

2.1. Materials and equipment

All chemicals used in the present work were of analytical grade. Benzene, 1-butanol, 2-pentanone, 1-nitropropane and pyridine were purchased from Alfa Chemical Co., Ltd (Tianjin, China). Naphthalene, acenaphthene, fluorene, dimethyl phthalate, diethyl phthalate, *n*-undecane, *n*-dodecane, *n*-tridecane, *n*-tetradecane and *n*-pentadecane were purchased from Sigma–Aldrich (St. Louis, USA). Bromobenzene, 1,2-dichlorobenzene, 1-bromodecane, 1,2,4-trichlorobenzene, 1,6-dibromohexane, methyl hexanoate, 2-octanone, benzyl chloride, ethyl benzoate and dicyclohexylamine were purchased from Beijing Chemical Reagent Company (Beijing, China). All analytes were dissolved in dichloromethane for GC separations.

Untreated fused-silica capillary tubing (0.25 mm, i.d.) was purchased from Yongnian Ruifeng Chromatogram Apparatus Co., Ltd. (Hebei, China). A HP-5MS capillary column (10 m × 0.25 mm, i.d., 0.25 μm film thickness, 5% phenyl polysiloxane) from Agilent Technologies was also used for comparison. An Agilent 7890A gas chromatograph equipped with a split/splitless injector, a flame ionization detector (FID) and an autosampler was used for GC separations. All the separations were performed under the following GC conditions: nitrogen of high purity (99.999%) as carrier gas at a flow rate of 1 mL/min, injection port at 300 °C, split ratio at 30:1, FID detector at 300 °C. Oven temperature programs for each separation were individually provided in their figure captions.

2.2. Capillary column preparation

Graphene used in this work was prepared by a facile hydrothermal strategy as described in Ref. [12] and in our previous work [13]. The as-prepared graphene was characteristic of few-layer stacked graphene sheets with highly three-dimensional cross-linking porous structure. Before static coating, a fused-silica capillary (10 m long × 0.25 mm i.d.) was flushed with dichloromethane for 0.5 h and after the solvent was removed, the capillary was purged with nitrogen at 260 °C for 2.5 h. Afterwards, the capillary column was pretreated with a saturated solution of sodium chloride in methanol and statically coated with a dispersion of graphene in dichloromethane (0.065%, w/v). This concentration was adopted after several trials, and higher concentration than this would result in column blocking. The reason for this is given as follows: The graphene used in this work had an average density of 0.23 g/cm³, about 4–5 times lower than those of polysiloxanes. Basically, for a given amount of stationary phase, a phase with lower density and larger surface area will have a larger volume. For such a stationary phase, therefore, only a low concentration could be used for the column coating. After the dispersion was injected into the capillary column, one end of the capillary column was sealed and the other end was connected to a vacuum system to gradually remove the solvent at 40 °C. After this, the coated capillary column was conditioned from 40 °C (30 min) to 180 °C at 1 °C/min and held at the high-end temperature for 7 h under a constant flow of nitrogen at 1 mL/min. Finally, the capillary column coated with graphene sheets was ready for GC separations.

3. Results and discussion

3.1. Column efficiency and McReynolds constants

Column efficiencies expressed as the number of theoretical plates per meter were determined by isothermal determination of *n*-dodecane at 120 °C at different flow rates. Effect of flow rate

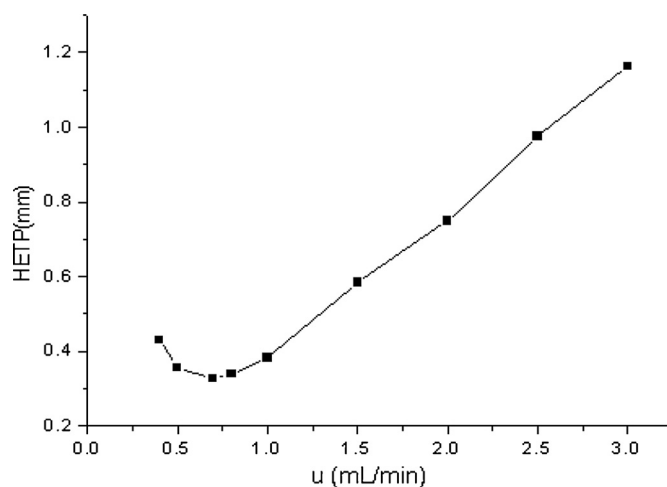


Fig. 1. Effect of flow rate on HETP of graphene column.

Table 1

McReynolds constants of graphene and HP-5MS capillary columns.

Stationary phase	X'	Y'	Z'	U'	S'
I for graphene	689	705	689	772	794
I for squalane	653	590	627	652	699
I for HP-5MS	686	662	693	751	766
ΔI for graphene	36	115	62	120	95
ΔI for HP-5MS	33	72	66	99	67

X', benzene; Y', 1-butanol; Z', 2-pentanone; U', nitropropane; S', pyridine. Temperature: 120 °C.

on the height equivalent to a theoretical plate (HETP) is shown in Fig. 1. As shown in the figure, the minimum height was achieved at 0.7 mL/min, corresponding to column efficiency of 3100 plates/m. As can be seen in the figure, column efficiencies varied less over the range of 0.5–1 mL/min. In this work, 1 mL/min was adopted for the subsequent separations so as to achieve good resolution in short run time.

McReynolds constants for graphene column were also determined at 120 °C, using five probe analytes, namely benzene, 1-butanol, 2-pentanone, 1-nitropropane and pyridine. A GC stationary phase with McReynolds constants less than 100 can be generally characterized as nonpolar or weakly polar stationary phase. As shown in Table 1, graphene column exhibited weakly polar nature. Noteworthy, graphene stationary phase had larger Y' and U' values than the conventional phase, suggesting its slightly stronger H-bonding and dipole–dipole interactions. This may stem from the possible presence of residual oxygen-containing groups such as hydroxyl and epoxy groups in the graphene product since it is almost impossible to remove all oxygen-containing groups in the reduction of graphene oxide.

3.2. Separation performance

Evaluation of the separation performance of graphene stationary phase was performed in comparison to a commercial HP-5MS column. In view of the solid type of graphene as GC stationary phase, initially, we also tried to employ a commercial Carbon-Plot column (15 m × 0.32 μm, i.d., 1.5 μm coating thickness, Agilent Technologies) coated with carbon-based type stationary phase for comparison. However, it did not allow resolution for the analytes, most of which did not elute out of the column, the analytes did elute exhibited poor resolution from each other possibly due to their strong adsorption of the analytes on the CarbonPlot column. For this reason, we finally employed a HP-5MS column instead. The obtained results are shown in Figs. 2–5, respectively.

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