研究快报

Hydroxy-Dibenzo Crown Ether Stationary Phase for Capillary Gas Chromatography Using Sol-Gel Technology

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Abstract: A new kind of crown ether, OH-dibenzo-14-crown-4 (OH-DB14C4), is prepared and coated onto the fused silica capillary by sol-gel process. Chromatographic characteristics including column efficiency (> 3 000 plates/m), thermal stability (to 330 ℃) and ability of deactivation are studied. The selectivity of new stationary phase is superior to sol-gel OH-terminal silicone oil (OH-TSO) for positional isomers of some aromatic compounds such as xylene, dichlorobenzene, nitrotoluene, nitrochlorobenzene. The new stationary phase has high sample capacity for separation of small molecular mass compounds: low-molecular-mass alcohols, ethers and ketones, short-chain fatty acids and volatile amines.

Key words: capillary gas chromatography; sol-gel process; OH-dibenzo-14-crown-4; stationary phase
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1 Introduction

The application of sol-gel column technology is becoming increasing in analytical chemistry, because it effectively combines capillary surface treatment, deactivation, coating and stationary phase immobilization into one single step and provides efficient incorporation of organic components into the inorganic polymeric structures in solution under extraordinarily mild thermal conditions. During the sol-gel process, a liquid like colloidal suspension (sol) is produced by means of hydrolysis and condensation of silicon alkoxide precursors such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) under either acidic or alkaline condition. The sol is then transformed into a gel through gelation, aging, and drying. The inherent advantages of sol-gel technology are the following: (a) time-effective, (b) low processing temperature, (c) unique ability to achieve molecular level uniformity in the synthesis of organic-inorganic composites, and (d) strong adhesion of the coating to substrate due to chemical binding. In recent years, it has been utilized in high performance liquid chromatography[1], capillary gas chromatography[2], solid phase microextraction[3], capillary electrophoresis[4] and capillary electrochromatography[5]. Many efforts have been made to vary the components of sol-gel to increase the ability of separation.

Although most crown ethers have the cavity structure and strong electronegative effect of heteroatoms on the crown ether ring that is useful as chromatographic stationary phase, the synthesis of crown ether substituted stationary phases through polysiloxane and cross-linking is time-consuming and complex[6]. In this work, a new kind of crown ether, OH-dibenzo-14-crown-4 (OH-DB14C4) has been synthesized and coated onto the inner walls of capillary by bonding with glass matrix during the gel formation process in sol-gel process. The structure of the crown ether is shown in Fig. 1. The hydroxyl group is necessary for the binding. Because this new stationary phase combines the advantages of sol-gel technology and crown ether, the column is expected to have unique selectivity, high thermal stability, high sample capacity and significant ability of deactivation.

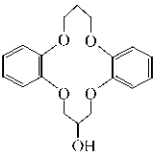

Fig.1 The structure of OH-dibenzo-14-crown-4

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2 Experimental

2.1 Reagents and apparatus

OH-terminal silicone oil (OH-TSO) was purchased from Chengdu Center for Applied Research of Silicone. Trifluoroacetic acid (TFA) was obtained from Beijing Chemical Factory. 3-(2,3-epoxyproxy)-propyltrimethoxysilane (PTMOS), tetraethoxysilane (TEOS) and poly (methylhydrosiloxane) (PMHS) were purchased from Wuhan University Chemical Factory. OH-dibenzo-14-crown-4 (OH-DB14C4) and dibenzo-propyl-15-crown-5 polysiloxane (PSO-DB-3-15C5) were synthesized by methods previously reported[7,8].

A Model SC-7 gas chromatograph (Sichuan Analytical Instrument Factory, China) equipped with a capillary split injection system and flame ionization detector was used throughout. A centrifuge Model LD4-2A (Beijing Medical Centrifuge Factory, China) was used to separate the sol solution from the precipitate. To mix various solution ingredients thoroughly, an ultrasonator Model SY-1200 (Shanghai Ultrasonic Instrument Factory, China) was used.

2.2 Preparation of sol-gel OH-DB14C4 column

To expose the maximum number of silanol groups on the silica surface, the fused silica capillary was first treated with 1.0 mol/L NaOH solution for 30 min and then washed with water for another 30 min. 0.1 mol/L HCl solution was used to neutralize the excess NaOH and the capillary was rinsed with water again. The columns were dried at about 120 ℃ for 2 h under a slow flow of nitrogen.

The sol solution for the OH-DB14C4 was prepared as follows: 0.025 g OH-DB14C4 was dissolved in 400 μL methylene chloride using an ultrasonator. A 20 μL volume of PTMOS and 20 μL of TFA were sequentially added with ultrasonic agitation for 20 min. Then 0.083 g OH-TSO, 0.028 6 g PMHS, 30 μL TEOS, and 30 μL TFA containing 5% water were added to the resulting solution, and the mixture was agitated for 5 min again. Then it was centrifuged for 5 min at the rotating rate of 2 500 r/min. The clear top portion of the resulting sol solution was introduced into the fused silica capillary, which was pretreated in previous steps, using a nitrogen pressure of 0.5 MPa. The excess sol was expelled from the column under the same nitrogen pressure after allowing it to stay inside the capillary for 30 min. The capillary column was then purged with nitrogen for 30 min, followed by temperature-programmed heating from 40 ℃ to 350 ℃ at a rate of 2 ℃/min under continued purging with nitrogen. The column was held under the final condition for 4 h.

Sol-gel OH-terminal silicone oil column (OH-TSO) was prepared in an analogous way.

3 Results and discussion

The chromatographic properties of sol-gel OH-DB14C4 and OH-TSO columns are demonstrated in Table 1. These three columns all have high column efficiencies (> 3 000 plates/m) and the reproducibility is good. This indicates that the sol-gel columns possess the good film-forming ability because of the addition of OH-TSO, which can help to spread the stationary phase on the column inner surface. The tailing factor (TF) for 1-octanol at 150 ℃ was close to 1.0 indicating the good deactivation of PMHS. Owing to the 3D network of sol-gel and the strong chemical bond between the stationary phase and the inner surface of capillary columns, the immobilization efficiencies of the columns still reached 90% after they were rinsed with 10 mL water and 10 mL methylene chloride, successively.

Table 1　Characteristics of sol-gel OH-DB14C4 and OH-TSO columns

Stationary phase	Column size ($l \times$ i.d.) (m × mm)	Capacity factor, k[1] (naphthalene at 130 ℃)	Column efficiency (plates/m)	TF	Immobilization efficiency[2] (%)
OH-DB14C4	10 × 0.25	9.64	3 900	1.01	93.4
OH-DB14C4	5 × 0.25	9.60	3 630	1.01	94.1
OH-TSO	7 × 0.25	9.47	3 132	1.02	95.1

1) $k = (t_r - t_o)/t_o$; t_o was determined directly with methane.

2) Immobilization efficiency = k_2/k_1; k_1, k_2 are the values of k before and after the columns were rinsed with solvent.

The Grob test mixture showed symmetrical peaks for both polar and apolar components of the mixture on sol-gel OH-DB14C4 and OH-TSO column indicating that the sol-gel stationary phases have rendered the capillary walls inert. The elution sequence of Grob test mixture on OH-DB14C4 column was *n*-decane → *n*-undecane → *n*-dodecane → 1-octanol →

3-butanediol → naphthalene → 2, 6-dimethylphenol → 2, 6-dimethylaniline. The elution order of 1-octanol and 1, 3-butanediol on OH-TSO column reversed with that on OH-DB14C4 column, which ascribes to the strong hydrogen-bonding force of crown ethers to alcohols.

Owing to the 3D network, sol-gel process provides enhanced surface area and thus increases sample capacity for the separation of some small molecular mass compounds such as low-molecular-mass alcohols , ethers and ketones, short-chain fatty acids (Fig. 2) and volatile aniline (Fig. 3). It is notable, free fatty acids are difficult to separate on GC with conventional column technology because of their high polarity. They are frequently converted into volatile derivatives of lower polarity. However, incomplete derivatization of these compounds may introduce significant error in their quantitation and complete derivatization is time-consuming and difficult. In this application, sol-gel OH-DB14C4 stationary phase provides perfect separation of volatile acids without derivatization. Fig. 3 shows the symmetrical peak shapes for volatile amines on sol-gel OH-DB14C4 column. Basic compounds are especially prone to tail on a poorly deactivated column. PMHS used in sol-gel process is a well-known surface deactivation reagent that contains chemically reactive hydrogen atoms for effective deactivation of silanol groups at elevatedemperatures, Therefore, there are no interactions between the acidic surface silanol groups and basic amine.

The sol-gel column technology enhanced thermal stability through the formation of strong chemical bonds between the OH-terminated stationary phase and the surface-bond silica substrate. Fig. 4 shows the separation of the phthalic diesters on sol-gel OH-DB14C4 column. They are separated well and have insignificant baseline drift during temperature programming to 330 ℃.

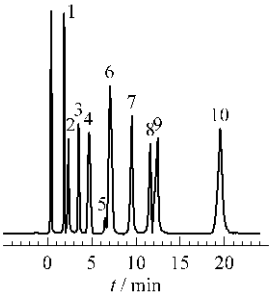

Fig. 4 Chromatogram of phthalic diesters

OH-DB14C4 column (5 m × 0.25 mm i.d.); temperature programming: from 240 ℃ to 330 ℃ at 4 ℃/min.

Peak: 1. diethyl phthalate; 2. dibutyl phthalate; 3. diamyl phthalate; 4. di-isohexyl phthalate; 5. di-*n*-hexyl phthalate; 6. di-isooctyl phthalate; 7. di-*n*-octyl phthalate; 8. di-isononyl phthalate; 9. di-*n*-nonyl phthalate; 10. didecylphthalate.

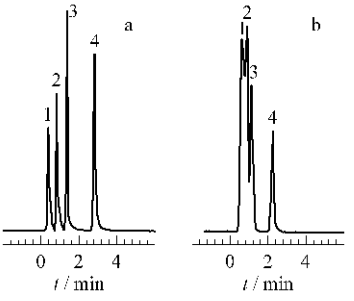

Fig. 2 Chromatogram of short-chain fatty acids

a. OH-DB14C4 column (5 m × 0.25 mm i.d.), b. PSO-DB-3-15C5 column (12.5 m × 0.25 mm i.d.); column temperature: 120 ℃.

Peak: 1. acetic acid; 2. propionic acid; 3. *n*-butyric acid; 4. *n*-caproic acid.

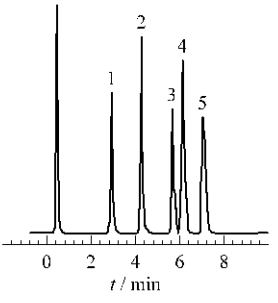

Fig. 3 Chromatogram of volatile amines

OH-DB14C4 column (10 m × 0.25 mm i.d.), column temperature: 140 ℃.

Peak: 1. aniline; 2. *o*-toluidine; 3. *m*-toluidine; 4. *N*-ethyl-*m*-toluidine; 5. *N*, *N*-dimethyl-*m*-toluidine.

Sol-gel OH-DB14C4 column shows good selectivity for positional isomers of aromatic compounds such as xylene, dichlorobenzene, nitrotoluene, nitrochlorobenzene. The capacity factors (k) and separation factors (α) for these four kinds of isomers on the sol-gel OH-DB14C4 column are greater than those on the sol-gel OH-TSO column. There is the possibility of dipole-dipole interactions between the polar groups of the test samples and crown ether stationary phase. Fig. 5 shows the separation of the isomers of xylene on sol-gel OH-DB14C4 and OH-TSO columns.

4 Conclusions

Acidic and basic compounds can be separated well on OH-DB14C4 stationary phase fabricated by sol-gel process, and it does not require additional derivatization step and has small tailing factor close to 1.0. Because of the chemical bonding between sol-gel coating and crown ether stationary phase, sol-gel-coated OH-DB14C4 column exhibits high thermal stability. It can be routinely used at 330 ℃ and has insignificant baseline

drift. Sol-gel coatings possess a porous structure and 3D network that provide high sample capacity for separation of small molecule compounds. Due to the cavity structure and strong electronegative effect of heteroatoms on the crown ether ring, it has unique selectivity for the separation of polar compounds such as positional isomers of aromatic compounds.

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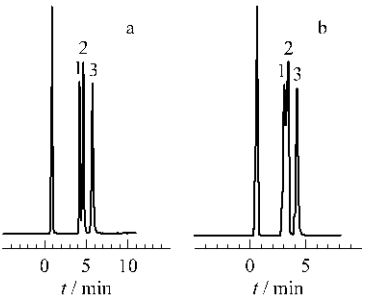

Fig.5　Chromatogram of isomer of xylene

a. OH-DB14C4 column (5 m × 0.25 mm i.d.), b. OH-TSO column (7 m × 0.25 mm i.d.); temperature: 80 ℃.

Peak: 1. *p*-xylene; 2. *m*-xylene; 3. *o*-xylene.

溶胶-凝胶法制备羟基苯并冠醚固定相用于毛细管气相色谱

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摘要:用溶胶-凝胶(sol-gel)技术制备了羟基-苯并冠醚毛细管气相色谱固定相,并测定了它的色谱性能。结果表明该柱具有柱效高(> 3 000/m)、热稳定性好(330 ℃)和去活能力强的优点。与溶胶-凝胶羟基硅油柱相比,该柱具有良好的选择性。一些芳香族位置异构体如二甲苯、二氯苯、硝基甲苯和硝基氯苯在溶胶-凝胶羟基-苯并冠醚柱上得到了很好的分离。该柱具有很高的柱容量,一些不能在冠醚聚硅氧烷上分离的小分子化合物,如小分子醇、酯、酮、短链脂肪酸和挥发性的胺,在溶胶-凝胶冠醚柱上有很好的分离。

关键词:毛细管气相色谱;溶胶-凝胶;羟基-二苯并冠醚;固定相