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Characterization of TiO₂/SiO₂ Based Stationary Phase for RP-HPLC

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Abstract: In this paper, we prepared a reversed-phase support by bonding octadecyltrichlorosilane onto TiO₂/SiO₂ particles, which were prepared by a layer-by-layer self-assembly technique and consists of micrometer-sized silica spheres as core and nanometer-sized titania particles as surface coating. The chromatographic behavior of the support was studied in detail. The support acted as a true reversed chromatographic stationary phase and had a hydrophobic selectivity. Further more, it had a comparable high carbon content of 11.51% and showed good stability in the basic solution of pH 10.

Keywords: Novel RP-HPLC packing, Octadecyl-bonded, TiO₂/SiO₂, Nanoparticle, Layer-by-layer self-assemble

INTRODUCTION

The study of titanium dioxide (titania) as a sorbent in normal phase, reversed-phase, and ion exchange liquid chromatography has been reported.^[1–5] It

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possesses the desirable mechanical and physical properties of silica and a chemical stability superior to those of silica.^[6–8] Titania is virtually insoluble in acids and alkalis, which enables separations to be performed at extreme pH values. Moreover, it is an amphoteric metal oxide, which has anion exchange properties at alkaline pH.^[9]

Though its applications in HPLC have been widely investigated, the accessibility and variability of specific surface area and particle size are much lower with titania than with silica.^[2,6,10–12] We had prepared a novel support material that consists of a full titania surface and could provide the merits of a good HPLC material; namely, it should have high specific surface area and pore volume, as well as excellent chemical stability. The molecular layer-by-layer (LbL) self-assembly technique had been used and achieved this goal.^[13] The basis of this approach is the electrostatic attraction between the charged species deposited. In this paper, the novel support material, $\text{TiO}_2/\text{SiO}_2$ was modified with octadecyltrichlorosilane and the preparation and evaluation of this packing were presented.

EXPERIMENTAL

Chemicals and Materials

Silica spheres were synthesized by the polymerization induced colloid aggregation (PICA) method in our laboratory. The average particle size was 6 μm . The specific surface area, pore volume, and pore diameter were 110 m^2/g , 0.21 cm^3/g , and 13 nm, respectively (measured by nitrogen adsorption). Tetrabutyl titanate, chemical grade, was purchased from Shanghai Sanyou Reagent Factory (Shanghai, China) chemical grade. Acetic acid was purchased from Jiangsu Sanmu Group Chemical Factory (Jiangsu, China) and sodium dodecyl sulfate (SDS) from Xi'an Chemical Reagent Co. (Xi'an, China). Octadecyltrichlorosilane (Lancaster, UK) was chemical grade. Methanol, toluene, ethanol, and acetone (Tianjin No.2 Chemical Reagent Plant, Tianjin, China) were all analytical grade.

Titania Nanoparticle Multilayer on Micrometer-Sized Silica Particles ($\text{TiO}_2/\text{SiO}_2$)

The titled support was prepared by alternate adsorption of surfactant SDS and titania sol onto micrometer scale silica spheres. The driving force is primarily the electrostatic adsorption. The preparative process has three major steps associated with it. First, the surface of silica particles is treated prior to use. Silica spheres were washed with acid, alcohol, and deionized water successively, followed by vacuum drying. Second, the silica core particles are filmed with surfactant (SDS). The dried silica particles were added into a solution containing 0.025–0.05 mol L^{-1} SDS

for the adsorption of SDS onto the core particles to form a surfactant monolayer film, followed by a careful washing procedure to remove the physically adsorbed SDS. The SDS filmed SiO₂ (SDS/SiO₂) was dried. Third, depositing titania sol on SDS/SiO₂. Titania sol was prepared as follows: at ambient temperature, tetrabutyl titanate, acetic acid and ethanol (1:0.3:3.5, v/v) was mixed together and stirred for several minutes, and named as solution A. Ethanol and water (of the volume that tetrabutyl titanate needs to complete hydrolysis) was mixed at the volume ratio of 20:1, and named solution B. To the solution A, solution B was added slowly with vigorous stirring. After tetrabutyl titanate completely hydrolyzed, titania sol was formed. It is yellow and clear. SDS/SiO₂ was added into the titania sol and stirred for 3 h, the TiO₂/SDS/SiO₂ material was formed, and it was washed with ethanol and then dried.

The multilayer TiO₂/SDS/SiO₂ was prepared by repeating the second and the third procedures several times. After being sintered at 525°C to burn off organic constituents, multilayer TiO₂/SDS/SiO₂ was transferred to a surface multilayer nanometer-scale TiO₂ particles/core micrometer-scale SiO₂ particles (TiO₂/SiO₂). The LbL self assemble technique permits the fabrication of the desired layers of TiO₂ nanometer particles on the SiO₂ spheres.

Stationary-Phase Octadecyl-Bonded TiO₂/SiO₂

Octadecyl-bonded TiO₂/SiO₂ stationary phase was synthesized by a reaction between TiO₂/SiO₂ and octadecyltrichlorosilane. TiO₂/SiO₂ and octadecyltrichlorosilane were added to toluene, then continuously stirred and fluxed for 36 h. The products were carefully washed with toluene, methanol, and acetone, and dried in a vacuum oven until of constant weight. The resulting octadecyl-bonded TiO₂/SiO₂ was filled into a 150 × 4.6 mm i.d. stainless steel column at 40 Mpa pressure.

Instrumentation

Specific surface area, pore volume, and pore size were measured by nitrogen adsorption and desorption isotherms at 77 K using an ASAP2010 surface analysis instrument (Micromeritics). The topography of the particle was displayed by a JSE-5600 LV scanning electron microscopy. Elemental analysis was carried out with a Vaivo Element analysis instrument.

Chromatographic Conditions

The HPLC system consisted of a Waters 515 HPLC pump, 2487 dual λ absorbance detector, and a 7725i injector with a 20-μL loop. Chromatograms were recorded with a SePu 3000 workstation (www.SePu.net).

RESULTS AND DISCUSSION

Characterization of TiO₂/SiO₂ Particles and Octadecyl-Bonded TiO₂/SiO₂

Direct observation of the TiO₂/SiO₂ particle was provided by scanning electron microscopy (SEM) as shown in Figure 1; a uniform surface of TiO₂/SiO₂ particles is visual. The specific surface area, total pore volume, and average pore diameter of TiO₂/SiO₂ are 202.07 m²g⁻¹, 0.3628 cm³g⁻¹, and 7 nm, respectively, calculated using the standard BET method.^[18] Elemental analysis showed that the carbon amount of octadecyl-bonded TiO₂/SiO₂ is 11.51%. The specific surface area of a support is generally accepted as one of its most important chromatographic parameters. It will influence the carbon amount of the stationary directly and also the chromatographic behavior. Several teams reported on the preparation of porous titania. For most porous titania supports, surface areas are less than 110 m²g⁻¹ and the amount of bonded alkyl is small. From Table 1, we can see that the octadecyl-bonded TiO₂/SiO₂ we prepared has a large surface area, pore volume, and high carbon amount; this will be very useful for the chromatographic separation.

Hydrophobic Selectivity of Octadecyl-Bonded TiO₂/SiO₂

It is well known in reversed-phase liquid chromatography that, over a reasonable range in mobile phase composition, the capacity factor of a homologous series of solutes can be approximately described by:^[19]

$$\ln k' = a + b \cdot n_{\text{CH}_2} + c \cdot \varphi + d \cdot \varphi \cdot n_{\text{CH}_2} \quad (1)$$

Here, n_{CH_2} is the number of methylene groups, φ is the volume fraction of organic modifiers in the mobile phase, and a , b , c , and d are empirical

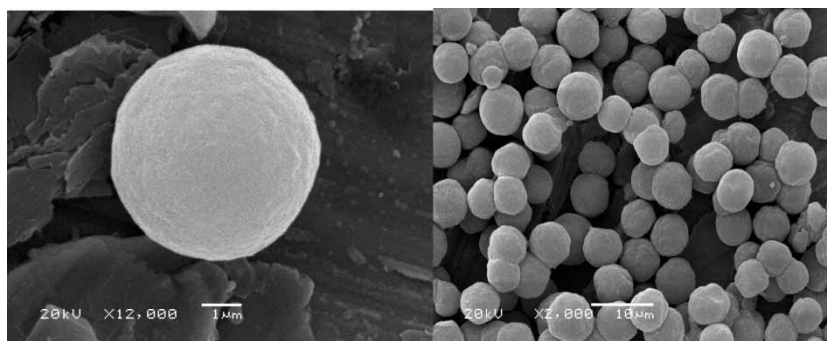


Figure 1. SEM image of TiO₂/SiO₂ particle.

Table 1. Parameters of octadecyl-bonded titania particles synthesized by different methods

Method	d _p /μm	a _s /m ² g ⁻¹	v _p /m ³ g ⁻¹	pd/nm	a _c	Ref.
LBL	6	202	0.36	7	11.51%	b
Sol-gel	4.5	34	0.22	26.4	3.3%	14
PICA	3.5	36.7	0.3	32.2	2.87%	15
Sol-gel	—	78	0.23	8	1.2–1.4 μmolm ⁻²	16
	4	126	0.3	11.1	6.16 %	17

a: d_p, particle diameter, a_s, surface area, v_p, pore volume, pd, pore diameter, a_c, carbon amount, b: this paper.

fitting coefficients. From this equation, we can derive several related equations under specific situations. First, when the composition of mobile phase is fixed, equation 1 becomes

$$\text{Ln}k' = (a + c \cdot \varphi) + (b + d \cdot \varphi)n_{\text{CH}_2} = A + B \cdot n_{\text{CH}_2} \quad (2)$$

A is the absolute retention, and the slope B is the hydrophobic selectivity.^[20,21] Equation 2 allows us to compare the absolute and relative retention of two stationary phases at a given mobile phase composition. In addition, the slope B is proportional to the free energy of transfer (ΔG°) per methylene group from the mobile phase to the stationary phase ($\Delta G^\circ = -BRT$; R is the gas constant, and T is the temperature).^[22] Equation 2 can be rewritten in a more conventional manner:

$$\text{Log} k' = \text{Log} k_0 + \beta \cdot n_{\text{CH}_2} \quad (3)$$

where $\log k_0$ is the absolute capacity factor of a homologous series of solutes; for the homologous series of benzene, $\log k_0$ is the capacity factor of benzene at the given mobile phase. β is the slope of the line, its value denotes the hydrophobic selectivity of the stationary phase.

At a fixed chromatographic condition, measuring the $\log k'$ of a homologous series of solutes such as the homologous series of alkylbenzene, then drawing the plot of $\log k'$ versus n_{CH_2} , we can obtain the slope of the plot β ; it is namely the hydrophobic selectivity of the stationary phase.

Using benzene, toluene, ethylbenzene, and cymene as solutes, 60%, 70%, 80% methanol as mobile phase, and measuring their $\log k'$ on the octadecyl-bonded TiO₂/SiO₂, we prepared, then drew the plot of $\log k'$ versus n_{CH_2} . Figure 2 shows the results of the plot. We can see that the plot has good linearity relativity. The hydrophobic selectivity of the stationary phase is 0.2138, 0.1841, and 0.1449, and the correlation coefficients are 0.9965, 0.9954, 0.9955 for 60%, 70%, and 80% methanol, respectively. These results demonstrated that the octadecyl-bonded TiO₂/SiO₂ we prepared is a good reverse-phase.

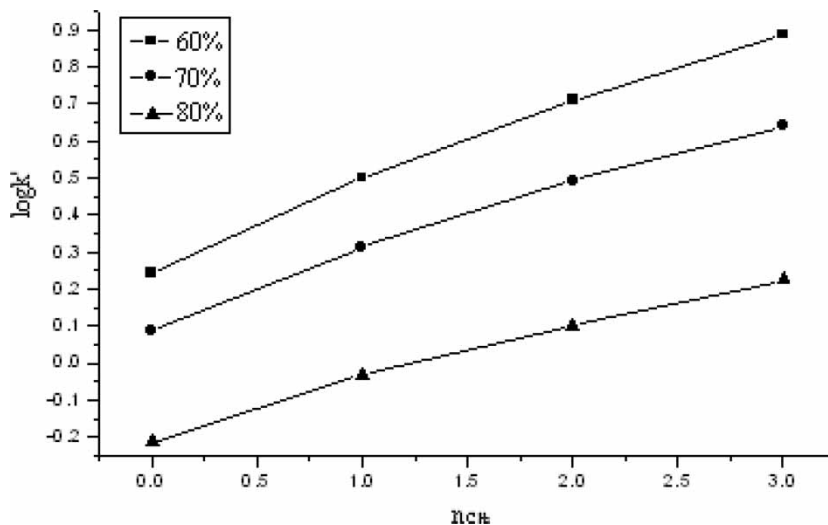


Figure 2. The plot of n_{CH_2} vs $\log k'$. Test solutes: benzene, toluene, ethylbenzene, Cymene 60% methanol; $\log k' = 0.2656 + 0.2138 \cdot n_{CH_2}$, $r = 0.9965$ 70% methanol; $\log k' = 0.1078 + 0.1841 \cdot n_{CH_2}$, $r = 0.9954$ 80% methanol; $\log k' = -0.1971 + 0.1449 \cdot n_{CH_2}$, $r = 0.9955$.

Sensitivity Octadecyl-Bonded TiO_2/SiO_2

When the solute is fixed, Equation 1 yields:

$$\ln k' = (a + b \cdot n_{CH_2}) + (c + d \cdot n_{CH_2})\varphi = C + D\varphi \quad (4)$$

where C is the intercept, and D is the slope related to the sensitivity of retention to the mobile phase composition. Equation 4 can be rewritten in a more conventional manner:^[23–27]

$$\log k' = \log k'_w - S \cdot \varphi \quad (5)$$

Here, k'_w is the extrapolated capacity factor of a solute when the mobile phase is pure water and S is $D/2.303$. Since k'_w refers to retention in pure water ($\varphi = 0$), it should be independent of the nature of the modifier. In general, this is not so when the value of φ is too small or too big, the plot of $\log k'$ versus φ is usually nonlinear. However, when the value of φ is between 0.1 and 0.9, equation 5 reflects the corresponding relativity between $\log k'$ and φ well. Therefore, we will use equation 5 to calculate the absolute mobile phase sensitivities.

The value of S is the sensitivity of the retention value for the solute to change in mobile phase composition on a given stationary phase. The bigger the value of S is, the stronger the retention value of the solute

influence by the polarity of the mobile phase. This is an important character of reverse-phase high performance liquid chromatography. We used benzene, toluene, ethylbenzene, and cymene as testing compounds, methanol and water of different volume fractions as mobile phase, and measured their $\log k'$ on octadecyl-bonded TiO₂/SiO₂ and drew the plot of $\log k'$ versus the volume fraction of methanol. The results are shown in Figure 3. We could see, from Figure 3, that the capacity factor of alkylbenzene compounds denotes good linearity relative to the volume fraction of methanol. For the compounds of benzene, toluene, ethylbenzene, and cymene, the relative coefficients were 0.9953, 0.9945, 0.9940, and 0.9868, respectively. The absolute mobile phase sensitivity of different compounds is obviously different. This demonstrates, again, that the octadecyl-bonded TiO₂/SiO₂ is a good stationary reverse-phase.

Stability Test

We used 65% methanol, consecutively flushing the column to a total of 3000 mL. Chromatograms of a mixture of solutes of alkylbenzene (benzene, toluene, ethylbenzene) were obtained periodically for every 500 mL. The result was shown in Figure 4a. The stability test in the basic solution was carried out by passing phosphate sodium solution (10 mmol L⁻¹, pH = 10)

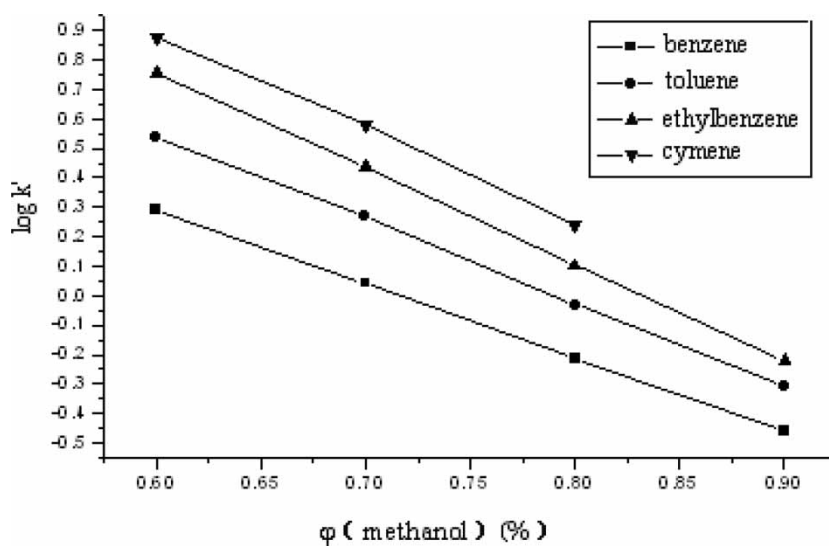


Figure 3. The effect of methanol volume fraction on $\log k'$. Benzene: $\log k' = 1.767 - 2.464 \varphi$, $r = 0.9953$, $s = 2.464$. Toluene: $\log k' = 2.21 - 2.787 \varphi$, $r = 0.9945$, $s = 2.787$. Ethylbenzene: $\log k' = 2.645 - 3.167 \varphi$, $r = 0.9940$, $s = 3.167$. Cymene: $\log k' = 2.847 - 3.24\varphi$, $r = 0.9868$, $s = 3.24$.

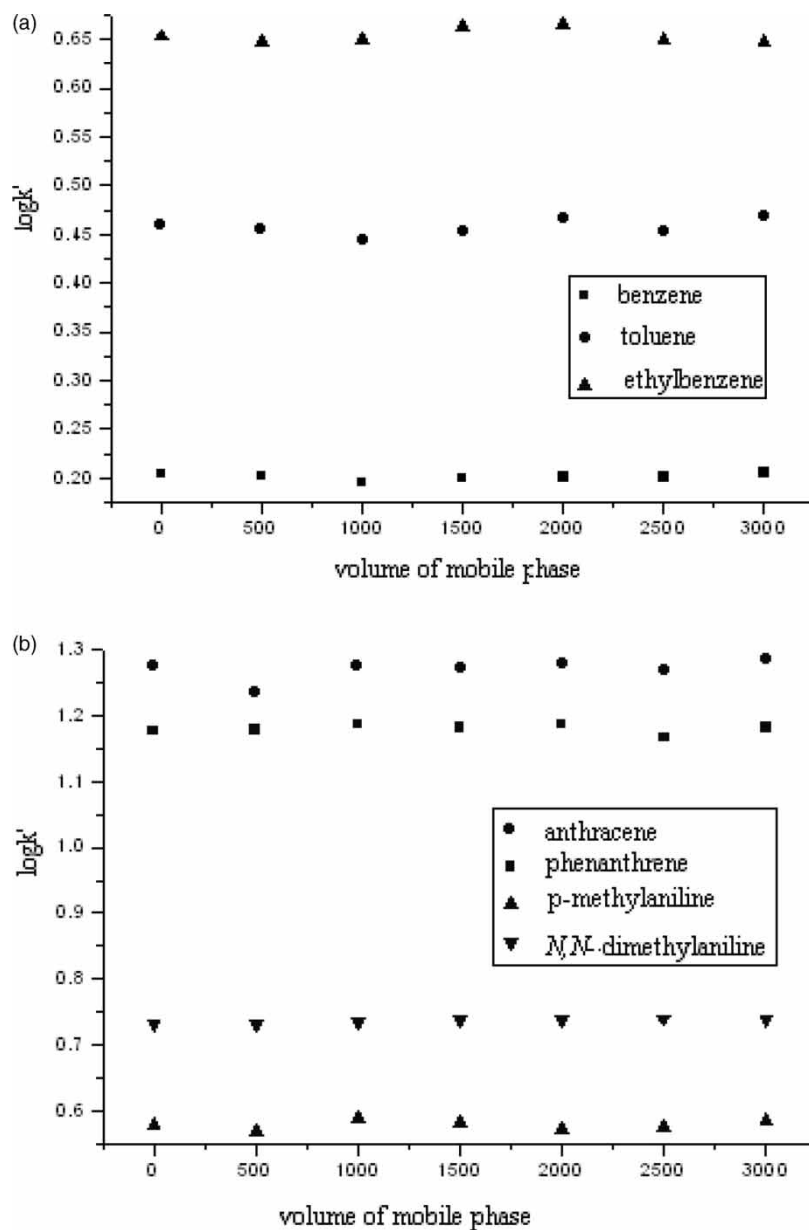


Figure 4. (a) Capacity factor of the test solutes versus the volume of neutral solution flushed through the column. Mobile phase: 65% methanol; flow rate: 1 mLmin^{-1} ; solute: benzene, toluene, ethylbenzene. (b) Capacity factor of the test solutes versus the volume of basic solution flushed through the column. Mobile phase: 10 mmolL^{-1} phosphate sodium solution at $\text{pH} = 10$; Flow rate: 1 mLmin^{-1} ; Solute: anthracene, phenanthrene, *N,N*-dimethylaniline, *p*-methylaniline.

through the column, at 0.7 mL/min⁻¹ to a total of 3000 mL. Chromatograms of a mixture of solutes (anthracene, phenanthrene, *N,N*-dimethylaniline and *p*-methylaniline) were obtained periodically with every 500 mL mobile phase flushing. Prior to each test, the column was conditioned with 70% methanol for 30 min. The basic stability of octadecyl-bonded TiO₂/SiO₂ phase is shown in Figure 4b. The results showed that octadecyl-bonded TiO₂/SiO₂ phases are stable up to pH 10 without any noticeable effect on the capacity factor or peak width of test solutes. This may be attributed to the presence of titania film and a crosslinked alkylpolysiloxane layer. The titania film demonstrated stability in basic solution, protecting the silica from dissolving; silicone rubber, which established a greasy layer or strong hydrophobic shield, protected the Ti-O-Si bonds from hydrolysis.

Chromatographic Studies

The column selectivity test is a useful tool for the characterization of octadecyl-bonded TiO₂/SiO₂. Alkylbenzene and aromatic compounds were tested. In Figure 6, benzene, toluene, ethenylbenzene, and cymene were separated well with a methanol-water ratio of 7:3, flow rate: 0.7 mL min⁻¹. The retention time increased with the increasing of the alkyl chain, proving that the alkyl chain is the main interaction center in the separation process.

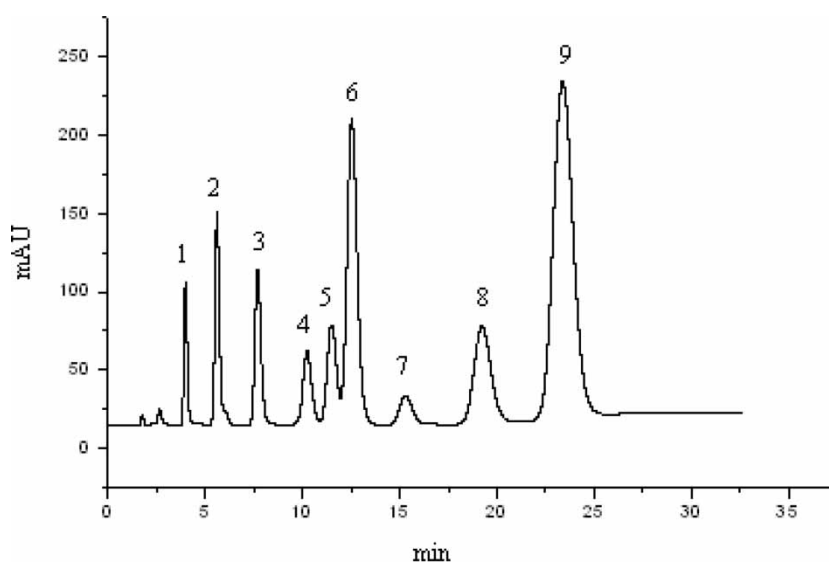


Figure 5. Chromatogram of the separation of aromatic compounds. Mobile phase: 70% methanol; Flow-rate: 0.7 mLmin⁻¹; 1. benzene, 2. toluene, 3. naphthalene, 4. cymene, 5. 2-methylnaphthalene, 6. biphenyl, 7. acenaphthene, 8. phenanthrene, 9. anthracene.

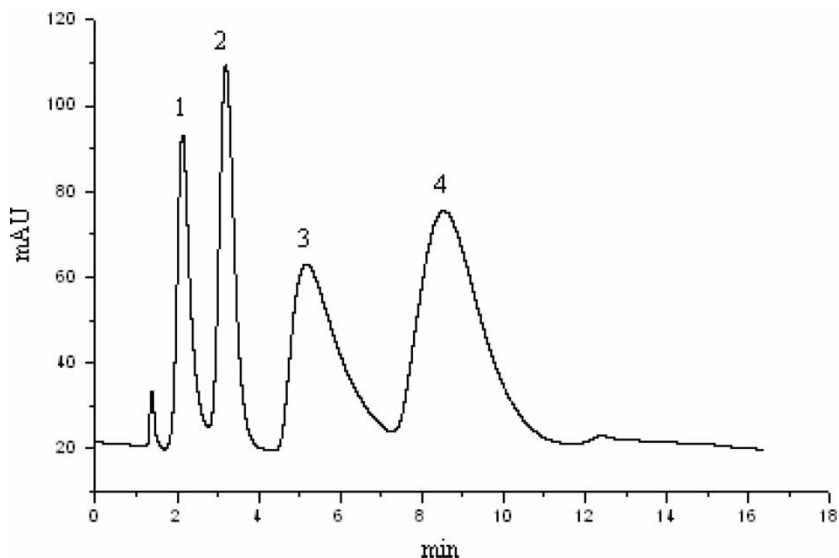


Figure 6. Chromatogram of the separation of basic compounds. Mobile phase: 55% methanol; Flow-rate: 0.9 mLmin^{-1} ; 1. *p*-nitroaniline, 2. *o*-nitroaniline, 3. aniline, 4. α -naphthylamine.

The reverse phase properties of octadecyl-bonded $\text{TiO}_2/\text{SiO}_2$ were verified, again, the results in Figure 5. An elution order in Figure 5 is from the least hydrophobic (benzene) to the most hydrophobic (anthracene).

The usefulness of octadecyl-bonded $\text{TiO}_2/\text{SiO}_2$ for the separation of basic compounds is demonstrated in Figure 6. A mixture of four basic compounds was well separated. We had separated *o*, *p*, and *m*-nitroaniline with the native $\text{TiO}_2/\text{SiO}_2$. Compared with the result in Figure 6, the elution order of *o*-nitroaniline and *p*-nitroaniline was reversed on octadecyl-bonded $\text{TiO}_2/\text{SiO}_2$, and it may attribute to the interaction of the alkyl chain.

CONCLUSION

In this study, a novel RP-HPLC support, octadecyl-bonded $\text{TiO}_2/\text{SiO}_2$, was prepared. It not only has a carbon amount higher than the conventional octadecyl-bonded titania but also was more stable than the conventional octadecyl-bonded silica. It will be a useful support for RP-HPLC. The retention characteristics and sensitivities of octadecyl-bonded $\text{TiO}_2/\text{SiO}_2$ have been determined. Results showed that it was a true reversed phase chromatographic stationary phase and had a hydrophobic selectivity. From the chromatographic behavior we concluded that it could be used to purify the basic and neutral compounds.

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REFERENCES

1. Winkler, J.; Marmé, S. *J. Chromatogr. A*. **2000**, *888*, 51–62.
2. Tani, K.; Suzuki, Y. *J. Chromatogr. A*. **1996**, *722*, 129–134.
3. Jaroniec, C.P.; Jaroniec, M.; Kruk, M. *J. Chromatogr. A*. **1998**, *797*, 93–102.
4. Yu, J.C.; Qu, F.; Lin, J.; Lam, H.L.; Chen, Z.L. *J. Liq. Chromatogr. & Rel. Technol.* **2001**, *24*, 367–369.
5. Nawrock, J.; Dunlap, C.; McCormick, A.; Carr, P.W. *J. Chromatogr. A* **2004**, *1028*, 1–30.
6. Kawahara, M.; Nakamura, H.; Nakajima, T. *J. Chromatogr.* **1990**, *515*, 149–158.
7. Trudiager, U.; Muller, G.; Unger, K.K. *J. Chromatogr.* **1990**, *535*, 111–125.
8. Tae-Young, X.; Kima, X. *J. Chromatogr. A* **2004**, *1047*, 165–174.
9. Kraus, K.A.; Phillips, H.O. *J. Am. Chem. Soc.* **1956**, *78*, 249–253.
10. Tani, K.; Suzuki, Y. *Chromatographia* **1994**, *38*, 291–294.
11. Yoshida, A.; Takahashi, K. *Chemitopia* **1994**, *15*, 18–29.
12. Pesek, J.J.; Matyska, M.T.; Ramakrishnan, X. *J. Chromatographia* **1997**, *44*, 538–544.
13. Dun, H.J.; Chen, L.R. *Anal. Chem.* **2004**, *76*, 5016–5023.
14. Murayama, K.; Nakamura, H.; Nakajima, T. *Microchem. J.* **1994**, *49*, 362–367.
15. Jiang, Z.; Zuo, Y. *Chinese J. Chromatogr.* **2001**, *19*, 297–300.
16. Trudiager, U.; Muller, G.; Unger, K.K. *J. Chromatogr.* **1990**, *535*, 111–125.
17. Ellwanger, A.; Matyska, M.T.; Albert, K. *Chromatographia* **1999**, *49*, 424–430.
18. Brunauer, S.; Emmett, P.H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.
19. Cozk, M.; Engelhardt, H. *Chromatographia* **1989**, *27*, 5–14.
20. Karger, B.; Gant, J.R.; Hartkopf, A.; Weiner, P.H. *J. Chromatogr.* **1976**, *128*, 65–78.
21. Vigh, G.; Varga-Puchony, Z. *J. Chromatogr.* **1980**, *196*, 1–9.
22. Melander, W.R.; Horvath, Cs. *Chromatographia* **1982**, *15*, 86–90.
23. Jandera, P.; Churacek, J. *J. Chromatogr.* **1974**, *91*, 207–221.
24. Tijssen, R.; Billeiet, H.A.H.; Schoenmakers, P.J. *J. Chromatogr.* **1976**, *128*, 65–78.
25. Schoenmakers, P.J.; Billeiet, H.A.H.; Tijssen, R.; de Galan, L. *J. Chromatogr.* **1978**, *149*, 519–537.
26. Jandera, P.; Churacek, J. *Advances in Chromatography*; Giddings, J.C., Ed.; Marcel Dekker: New York, 1981; Vol. 19, 125–260.
27. Jandera, P.; Churacek, J.; Svoboda, L. *J. Chromatogr.* **1979**, *174*, 35–50.

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