Chromatographic evaluation of radiation-immobilized poly(methyloctylsiloxane) on titanium-grafted silica

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Abstract

Silica was chemically modified by reaction with titanium tetrachloride to give a titanium-grafted silica (Si–Ti). Poly(methyloctylsiloxane) (PMOS) was sorbed into the pores of this support, which was then γ-irradiated (80–120 kGy) and extracted with dichloromethane. Chromatographic performance of the stationary phase was evaluated in terms of the efficiency (plates/m), resolution (R_s), retention factor (k) and asymmetry (A_s) of a standard mixture of solutes of different polarities. γ-Irradiation increases the quantity of retained PMOS and the efficiency of the resulting columns. These stationary phases, initially loaded with 50% PMOS following titanium-grafting, retained $32\pm2\%$ of the PMOS. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over 75% of high-performance liquid chromatography (HPLC) separations are carried out using silica gel-based packing materials. Silica is popular as a support material because of the wide variety of available pore diameters, the uniformity of the pores, the high specific surface areas and the ease with which many stationary phase materials can be bonded to its surface [1]. On the other hand, silanol groups that are not removed or covered may cause tailing or irreversible adsorption of some basic solutes, while the silica base material tends to dissolve rapidly in aqueous solutions at pH values higher than 7 [2].

Many approaches have been considered for overcoming the limitations of silica at high pH [3]. Most or all of these involve the concept of a protective layer for covering, hence protecting, the silica surfaces from undesirable interactions with the mobile phase. Organic polymeric materials are usually used, in various ways, to accomplish this objective [3]. Nevertheless, the requirement of complete coverage, to obtain complete protection, is a difficult one to attain.

An alternative tactic, which has not yet been fully explored for chromatographic purposes, is to permanently alter the silica surface by chemical incorporation ("grafting") of metal oxide materials known for their high stability in high (and in low) pH environments onto the silica surface. Procedures for the grafting of such materials onto a silica (SiO_2) surface have been described for the case of titanium (TiO_2), zirconium (ZrO_2) and other oxides [4–6]. The present paper is a preliminary study of the feasibility of using titanium modified (grafted) silica for HPLC.

A basic assumption at the beginning of this work involving a grafted oxide is that the physical–chemi-

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cal interactions of the resulting surface should be either very similar to those of the pure guest oxide or between those of the host silica and the guest oxide. The chromatographic literature reports that porous TiO_2 particles have been prepared and tested for direct use in normal-phase HPLC [7–9] and as support particles for bonded reversed-phase [9–15] and ion-exchange HPLC [9,16]. In the normal-phase mode, basic solutes have been rapidly separated with symmetrical peaks but acidic solutes tend to elute slowly and have relatively poor peak shape [7–9]. The few reports on HPLC phases bonded onto a TiO_2 support show that the TiO_2 surface can indeed support phases such as octadecyl, prepared by re-action of the titania surface with *n*-octa-decyltriethoxysilane [11,12] and by a silanization/hydrosilation bonding method [13,14] that yields reversed-phases stable even under extremes of pH.

In the present paper we explore whether titanium oxide grafted onto silica (Si–Ti) can support a sorbed/immobilized stationary phase such as poly-(methyloctylsiloxane) (PMOS) for HPLC separations.

2. Experimental

2.1. Reagents and materials

Davisil-630, an irregular silica having a mean particle size (d_p) of 10 μm and a specific surface area of 380 m^2 g^{-1}, was obtained from Alltech. PMOS (product PS-140 from Petrarch Systems/Hüls America) has a mean molar mass of 6200. Analytical-reagent grade or HPLC-grade solvents were obtained from Merck (dichloromethane, carbon tetrachloride, chloroform, acetone, benzonitrile, benzene, toluene and naphthalene) or Mallinckrodt (methanol). Titanium tetrachloride, $TiCl_4$, was obtained from Aldrich. Water was distilled then purified in a Milli-Q system from Millipore.

2.2. Synthesis of titanium-modified silica (Si–Ti)

Silica activated at 110°C under vacuum was immersed in toluene (previously dried) and titanium tetrachloride was added in a ratio of 1.0 mmol Ti/g

SiO_2. The mixture was refluxed for 12 h under an atmosphere of argon. After that, the resulting material was washed with toluene to remove any excess of $TiCl_4$, filtered and heated to 110°C under vacuum. Then, ammonium gas was passed through the dried material for 3 h after which the material was washed with ethanol and filtered. Finally, the material was hydrolysed with 10^{-3} mol l^{-1} nitric acid, washed several times with water to remove all chlorides from the surface of the support and finally dried at 110°C for 24 h before use.

2.3. Preparation of the stationary phase

Equal masses of Ti–Si and PMOS were added to dichloromethane by first dissolving the PMOS in the solvent, then stirring in the dried support. This mixture was stirred for 3 h at room temperature and the dichloromethane was then removed by evaporation to obtain the stationary phase (Si–Ti/PMOS) with a 50% PMOS nominal loading. Once the Si–Ti/PMOS stationary phase had been prepared, samples of 3.0 g were sealed in glass ampoules under air, then irradiated to 80 or 120 kGy of absorbed dose from an industrial ^{60}Co γ-ray source (IBRAS-CBO, Campinas, Brazil) at a dose rate of ~40 kGy h^{-1}. Portions of irradiated packing material were then extracted with CH_2Cl_2 at reflux temperature for 6 h, then allowed to dry at ambient temperature prior to heating for 24 h at 110°C. The columns, 150×3.8 mm, made from locally purchased type 316 stainless steel tubing with highly polished internal surfaces, were downward packed at 42 MPa with a Haskel packing pump using 10% slurries of the packing material in CCl_4 or in $CHCl_3$–MeOH (90:10, v/v), using methanol as the propulsion solvent. Table 1 lists the columns prepared from the different stationary phases.

2.4. Physical characterization

Elemental analyses for carbon (%) were obtained on a Perkin-Elmer Model 2400 CHN analyzer. The quantity of PMOS (%) was then calculated using the following equations:

$$\% \text{ C} = (w_C/w_{\text{sample}}) \times 100$$

Table 1
Column identifications

Column	Initial PMOS loaded (%)	Stationary phase			
		Support	Irradiation dose (kGy)	Extraction	Slurry solvent
0	50	SiO_2	None	No	CCl_4
1	50	Si–Ti	None	No	CCl_4
2	50	Si–Ti	80	No	CCl_4
3	50	Si–Ti	120	No	CCl_4
4	50	Si–Ti	120	Yes	CCl_4
5	50	Si–Ti	80	No	$CHCl_3$–MeOH

where w_C = carbon mass and

$$w_{sample} = w_{support} + w_{PMOS} = \text{mass of sample}$$

Since 62% of the polymer mass refers to carbon,

$$w_{PMOS} = (w_C / 0.62):$$

$$\% \text{ PMOS} = (w_{PMOS} / w_{sample}) \times 100$$

Quantification of Ti(IV) was obtained by X-ray fluorescence using a Tracer Model Spectrace 5000. The calibration curve was prepared using mixtures of purified silica and TiO_2 (Riedel-de Haën) containing from 1 to 10% (w/w) Ti. Mean pore diameter (d_p) and specific pore volumes (V_p) for the packing material was determined by mercury intrusion using a Model 9310 Micromeritics Instrument.

Quantification of hydroxyl groups were carried out by potentiometric titration using 0.5 g of material suspended in 10 ml of a 10% aqueous solution of NaCl and titrated with 0.0100 mol l^{-1} NaOH to pH 9 [17].
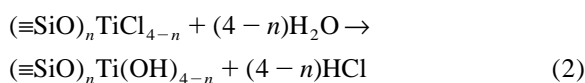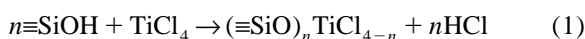
2.5. Chromatographic measurements

Reversed-phase column testing was done with a system consisting of a Shimadzu LC-10AD pump, a Shimadzu Model SPD-10AV UV–Vis absorbance detector, a Rheodyne Model 7125 injector (5 μl loop) and a Hewlett-Packard Model 3396 integrator. The velocity of the integrator paper was usually 0.5 cm min^{-1} but a paper velocity at 2.0 cm min^{-1} was used when performance calculations were to be made. All measurements were carried out at ambient temperature using a methanol–water (70:30, v/v) mobile phase at a flow-rate of 0.3 ml min^{-1}, near the

optimal flow-rate as determined by a van Deemter plot. Chromatographic performance was evaluated by means of the efficiency (plates/m), retention factor (k), resolution (R_s), separation factor (α) and asymmetry (A_s), manually determined from the chromatograms for naphthalene or the toluene–naphthalene pair, as appropriate. The asymmetry was measured at 10% of the peak height [18]. The time for passage of the mobile phase through the column, t_M, was determined from the refractive index deviation obtained by injection of pure methanol.

3. Results and discussion

The modification process can be represented by the following equations:

$$n \equiv SiOH + TiCl_4 \rightarrow (\equiv SiO)_n TiCl_{4-n} + nHCl \qquad (1)$$

$$(\equiv SiO)_n TiCl_{4-n} + (4-n)H_2O \rightarrow$$
$$(\equiv SiO)_n Ti(OH)_{4-n} + (4-n)HCl \qquad (2)$$

where ($\equiv$SiOH) stands for the silanol groups.

The amount of titanium-grafted to the silica, as determined by X-ray fluorescence spectroscopy, was $5.1 \pm 0.2\%$. Table 2 shows the specific surface area (S_{BET}), pore volume (V_p) and surface concentration of available hydroxyl groups for bare silica, the titanium-grafted silica particles and the stationary phase with PMOS. Both the surface area and the quantity of titratable hydroxyl (titanol and silanol) groups decreased with the titanium modification. The sorption of PMOS also resulted in a significant decrease of specific area as a result of loading PMOS into the pores of the support.

Table 2
Physical and chemical characteristics of bare silica and titanium-modified silica (Si–Ti)

Sample	S_{BET} (m^2 g^{-1})	Hydroxyls (mmol g^{-1})	V_p (ml g^{-1})
SiO$_2$	383	0.590	1.05
Si–Ti	274	0.443	1.17
Si–Ti/PMOS	106	0.095	–

The chromatographic parameters obtained with a test mixture for the several columns (Table 1), having PMOS sorbed and/or immobilized onto the titanium-modified silica, with or without post-irradiation extraction with CH$_2$Cl$_2$, after two different doses of γ-irradiation, are shown in Table 3. These parameters indicate good separation and interaction of the test compounds with the liquid stationary phase. Typical separations are shown in Fig. 1. The decrease in peak asymmetry with radiation suggests that crosslinking occurs between the chains of the polymer, reducing the contact of the solutes with the chromatographic support. Neither γ-irradiation nor extraction significantly affected efficiency. The slurry solvent (CHCl$_3$–MeOH, 90:10, v/v) produced columns with similar chromatographic parameters to those produced with the same stationary phase using CCl$_4$ as the slurry solvent.

Although γ-irradiation does not significantly affect the column efficiency, it is very important in increasing the amount of polymer immobilized onto the chromatographic support, as is indicated in Table 4. The packing material that was not submitted to any treatment retained about 22% of PMOS, similar to

that retained under similar conditions on pure silica [19]. The packing material submitted to γ-radiation retained about 32% of the PMOS, presumably as a result of crosslinking of the PMOS. The irradiation dose does not appear to affect the amount of PMOS retained but the column prepared from packing material which received the lower dose (80 kGy) shows better efficiency. Similar crosslinking behavior of PMOS was observed by Schomburg et al. [20]. The increased amount of immobilized polymer after γ-irradiation could lead to increase chemical stability in alkaline mobile phases, for the elution of basic solutes, as previously reported for silica supports [20].

4. Conclusions

Titanium-grafted silica is suitable for use as a chromatographic support for applications in reversed-phase HPLC. Results of both specific area and X-ray fluorescence determinations confirm the presence of titanium-grafted onto silica. γ-Irradiation increases the amount of PMOS retained on the Si–Ti

Table 3
Chromatographic parameters for PMOS sorbed or immobilized onto bare silica and Si–Ti

Stationary phase[a]	k[b]	k[c]	α[d]	R_s[d]	A_s[c]	N/m[c] (plates/m)
0	2.5	3.2	1.3	2.7	1.5	25.000
1	1.8	2.2	1.2	2.1	1.8	24.220
2	4.1	5.1	1.2	3.0	1.4	33.670
3	2.6	5.4	1.2	2.8	1.5	28.490
4	5.3	6.6	1.3	3.1	1.6	27.740
5	4.5	5.6	1.3	3.4	1.3	34.900

[a] Stationary phase as in Table 1.
[b] Calculated for toluene.
[c] Calculated for naphthalene.
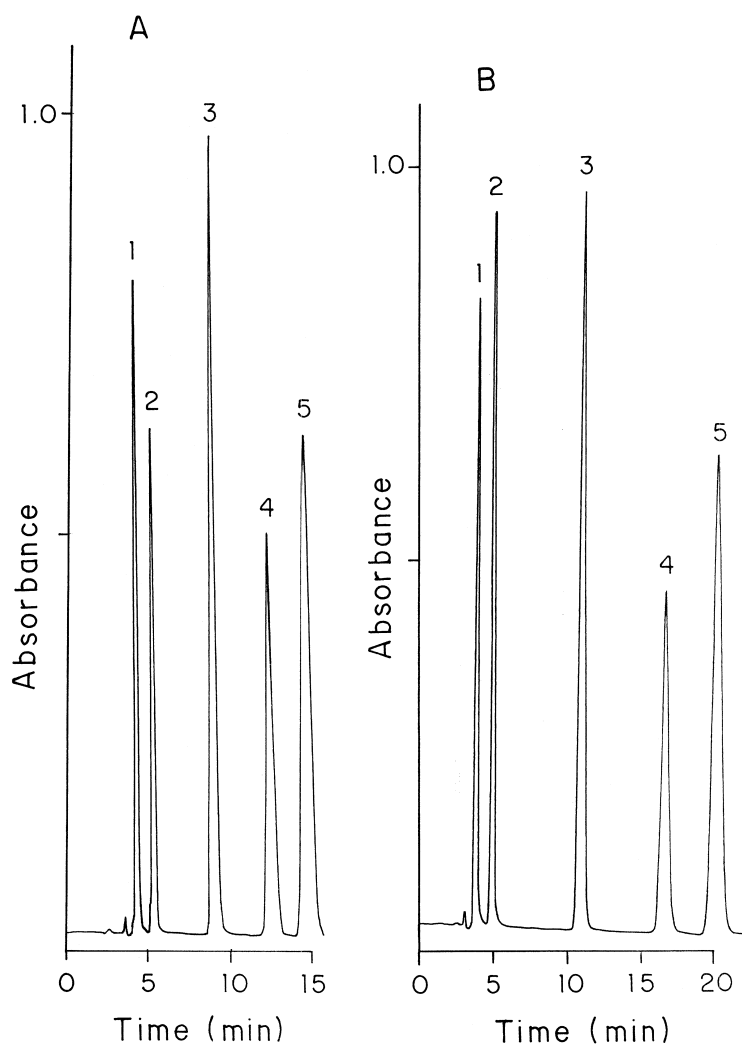[d] Calculated for toluene–naphthalene.

Fig. 1. Chromatogram obtained with column 1 (A) and column 5 (B). Conditions: mobile phase: MeOH–water (70:30, v/v), flow-rate: 0.3 ml min^{-1}, detection: UV, 254 nm, test solutes: (1) acetone, (2) benzonitrile, (3) benzene, (4) toluene and (5) naphthalene.

Table 4
Amount of PMOS (%) in the packing material

Column[a]	PMOS (%)[b]	
	After extraction in CH_2Cl_2	Packing material
0	–	25
1	–	22
2	–	32
3	–	32
4	33	33
5	–	32

[a] Stationary phase: as in Table 1.
[b] Initial PMOS (50%).

support and improves the chromatographic performance.

Acknowledgements

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