Evaluation of the stability of polymer-coated silica-based packing materials for high-performance liquid chromatography

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ABSTRACT

The stability of polymer-coated silica-based packing materials for high-performance liquid chromatography was examined. Linear relationships between the pH of the eluent and the logarithm of the concentration of silicic acid dissolved in the effluent, log C_{SIL}, were observed, and the slope of the lines was dependent on the surface properties of the packing materials. A lower solubility was observed for polymer-coated silica and glass beads in comparison with common porous bare silica beads. A linear relationship between the specific surface area and log C_{SIL} was observed for porous silica beads, and the plots for polymer-coated silica and glass beads deviated from linearity.

INTRODUCTION

Silica-based packing materials are widely used in high-performance liquid chromatography (HPLC) because of the high column efficiencies and wide applicability. However, silica-based packing materials are unstable in aqueous mobile phases, especially at high pH[1,2]. This drawback is overcome by employing polymer-based materials[3,4] or coating the silica gel surface with a layer of polymer[5-9], and such stationary phases are now commercially available. Another strategy for improving the stability of silica-based materials is to use an eluent saturated with silica. Other parameters affecting the stability involve flow-rate, temperature, eluent modifier, etc.[1,2].

This paper compares the stability of polymer-coated silica-based materials with that of common silica-based materials and glass beads under various operating conditions.

EXPERIMENTAL

Reagents

All of the reagents were of analytical-reagent grade from Wako (Osaka, Japan), unless indicated otherwise. Purified water was prepared by using a Milli-Q system (Nihon Millipore Kogyo, Tokyo, Japan). Molybdic acid and the reducing reagent solution for the detection of silicic acid were prepared as described previously[10]. The molybdic acid solution was prepared by mixing 8 ml of 10% (w/v) ammonium molybdate and 4 ml of 6 *M* hydrochloric acid, followed by dilution to 100 ml with purified water. The reducing reagent solution was prepared by mixing 8 ml of 10% (w/v) oxalic acid and 11 ml of 0.25% (w/v) 1-amino-2-naphthol-4-sulphonic acid (ANSA) solution, followed by dilution to 100 ml with purified water. The ANSA solution was prepared according to the proposed method[11] as follows: 0.5 g of 1-amino-2-naphthol-4-sulphonic acid and 2 g of sodium sulphite were dissolved in *ca.* 50 ml of purified water, mixed with 20 g of sodium sulphite dissolved in *ca.* 120 ml of purified water and diluted to 200 ml with purified water.

Silicon standard solution for atomic absorption spectrometry was obtained from Wako. Acetic acid and sodium acetate were used to adjust the pH of the eluent.

Equipment

A diagram of the detection system is shown in Fig. 1. The prepared molybdic acid and reducing reagent solutions were supplied via D and E, respectively. These reagents and the sample were supplied at 60 μl/min by using a single Minipuls 2 peristaltic pump (Gilson, Villiers le Bel, France). The sample solution was mixed with the molybdic acid solution to form yellow molybdosilicic acid during passage through the 8 m $\times$ 0.5 mm I.D. PTFE reaction tube (5 in Fig. 1) at room temperature. The yellow molybdosilicic acid was then converted into the blue molybdosilicate complex by reaction with the reducing reagent in the 5 m $\times$ 0.5 mm I.D. PTFE tube, followed by detection at 815 nm with a UVIDEC-100 III UV–visible spectrophotometer (JASCO, Tokyo, Japan). This system allows the detection of ionic monosilicate (or silicic acid).

The packing materials employed were Develosil (Nomura Chemical, Seto, Japan), Capcell C1 SG120 (Shiseido, Tokyo, Japan), non-porous glass beads
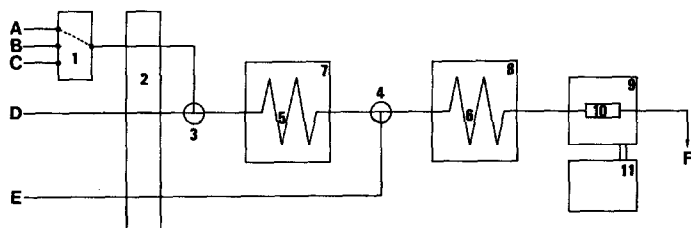

Fig. 1. Diagram of the apparatus. Equipment: 1 = sample exchange valve; 2 = peristaltic pump; 3, 4 = mixing joints; 5 = reaction tube for formation of molybdosilicic acid; 6 = reaction tube for formation of molybdenum blue; 7, 8 = aluminum block bath; 9 = spectrophotometer; 10 = flow cell (8 μl); 11 = recorder. Reagents: A = sample; B = blank; C = standard; D = molybdic acid solution; E = reducing reagent solution; F = waste.

(Whatman, Clifton, NJ, U.S.A.) and porous glass beads PSG-10μ (Fuji-Davison Chemical, Kasugai, Japan). Develosil and Capcell C1 SG120 are bare silica and polymer-coated silica beads, respectively. Develosil LOP ODS (Nomura Chemical) and Capcell C18 SG120 (Shiseido) were examined as examples of octadecyl-bonded silica gel. The base material of the latter is Capcell C1 SG120.

Table I lists the packing materials examined and their dimensional data as given by the manufacturers. The materials were packed into 50 mm × 4.6 mm I.D. columns by a dry packing method. The eluent was supplied at 0.5 ml/min by using an LC-6AD HPLC pump (Shimadzu, Kyoto, Japan), unless indicated otherwise. The effluent was sucked via A in Fig. 1.

RESULTS AND DISCUSSION

The detection system was evaluated by using the standard silicon solution and a calibration graph was prepared from steady-state signals. The steady-state signals were proportional to the concentration of silicon up to 1 ppm. The limit of detection was 1.6 ppb (10^9) at a signal-to-noise ratio of 3, and the relative standard deviation of the signal intensity was 1.0% for ten measurements of 10 ppb silicon. When the concentration of silicic acid in the effluent exceeded 1 ppm, the solution was appropriately diluted with purified water.

Fig. 2 demonstrates linear relationships between the pH of the eluent and the logarithm of the concentration of silicic acid in the effluent (log C_{SIL}) for bare silica gel, polymer-coated silica gel and glass beads. The concentration is expressed as ppm by weight of silicon (or μg/ml). The pH was adjusted with acetic acid and sodium acetate. As the dissolution behaviours of the packing materials were independent of the concentration of acetate in the eluent between 20 and 100 mM, 60 mM was adopted as the concentration of acetate throughout this work. For a series of porous bare silica beads, the slopes of the straight lines were nearly the same, and a material with a larger

TABLE I

PACKING MATERIALS EMPLOYED

Packing material	Type	Particle diameter (μm)	Pore size ($\mathring{A}$)	Specific surface area (m^2/g)
Develosil 30-5	Silica	5	30	704
Develosil 60-5	Silica	5	60	437
Develosil 100-5	Silica	5	100	324
Develosil 300-5	Silica	5	300	152
Develosil NP silica-5	Silica	4.5	NP[a]	0.6
Capcell C1 SG120	Silica	5	120	200
PSG-10μ	Glass beads	11.5	178	157
Glass beads (Whatman)	Glass beads	40	NP	–
Develosil LOP 60	Silica	30	60	500
Develosil LOP ODS	ODS	30	100	150
Capcell C18 SG120	ODS	5	120	140

[a] NP = non-porous.
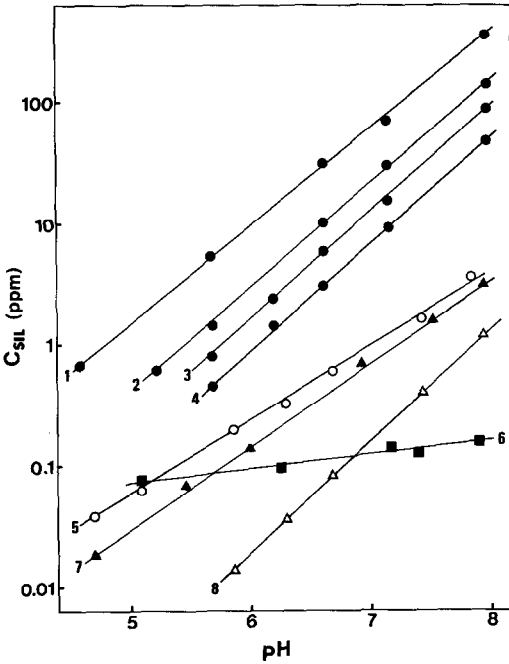
Fig. 2. Relationships between pH of the eluent and the logarithm of the concentration of silicic acid in the effluent (log C_{SIL}). Column, 50 × 4.6 mm I.D.; eluent, 60 mM acetate; flow-rate, 0.5 ml/min; column temperature, 20°C. Packing materials: 1 = Develosil 30-5; 2 = Develosil 60-5; 3 = Develosil 100-5; 4 = Develosil 300-5; 5 = Develosil NP silica-5; 6 = Capcell C1 SG120; 7 = PSG-10μ; 8 = non-porous glass beads (Whatman).
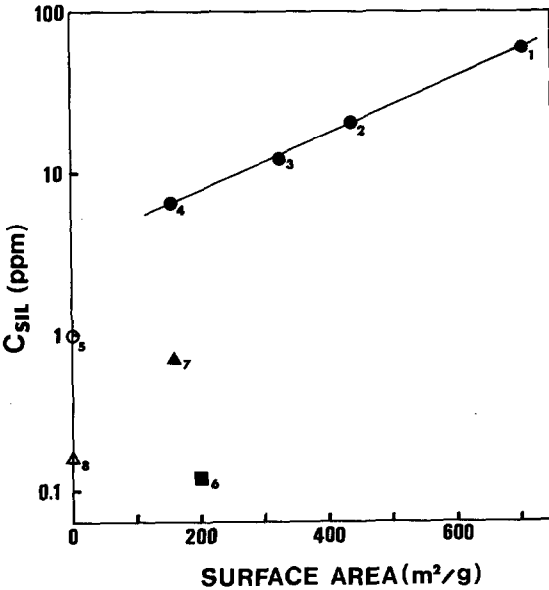

Fig. 3. Plots of log C_{SIL} as a function of specific surface area. Column, 50 × 4.6 mm I.D.; packing materials, as in Fig. 2; pH, 7.0; flow-rate, 0.5 ml/min; column temperature, 20°C.
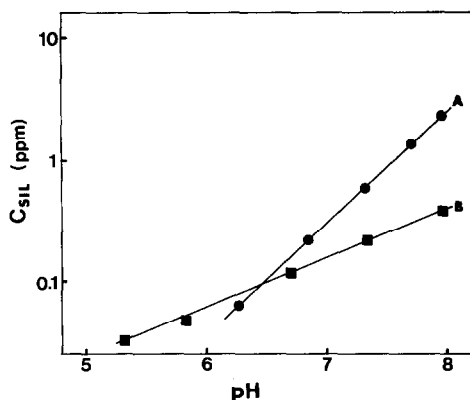
Fig. 4. Relationships between pH of the eluent and log C_{SIL} for ODS columns. Columns, 50 × 4.6 mm I.D.; (A) Develosil LOP ODS and (B) Capcell C18 SG120; eluent, 60 mM acetate; flow-rate, 0.5 ml/min; column temperature, 20°C.

specific surface area gave a larger log C_{SIL} value. A smaller dependence of the pH on log C_{SIL} was observed for the polymer-coated silica gel in comparison with other materials. The log C_{SIL} values for the polymer-coated silica gel were much lower than those of porous bare silica beads, especially at higher pH. Bleeding at a concentration of 10 ppm corresponds to the dissolution of 6.4 mg of silica gel for a 10-h operation.

Fig. 3 shows plots of log C_{SIL} versus specific surface area when the pH of the eluent was fixed at 7. The plots lie on a straight line for a series of porous silica beads. The plots for glass beads, polymer-coated silica gel and non-porous silica gel deviate from linearity. The largest deviation was observed for the polymer-coated silica gel, which may be the result of protection of the surface with a poly(dimethylsiloxane) film.

Column temperature, eluent flow-rate and eluent composition affected the dissolution behaviour. These effects were similar to those reported in the literature[1,2].

Fig. 4 illustrates linear relationships between log C_{SIL} and the pH of the eluent for ODS materials. The results shown in Figs. 2 and 4 indicate that the concentration of dissolved silicic acid is substantially decreased for Develosil LOP ODS in comparison with its original silica gel, whereas a large difference in the log C_{SIL} value is not observed between Capcell C18 SG120 and its base material, Capcell C1 SG120. The surfaces of Capcell C18 SG120 are coated with a poly(dimethylsiloxane) film, whereas Develosil LOP ODS is prepared from bare silica gel. The signal was enhanced when the effluents were treated with sodium hydrogencarbonate at elevated temperature. Such a treatment is recommended to allow the detection of soluble and/or colloidal species[11]. In addition, the signals for silica gel columns were not changed by the above treatment.

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