Evaluation of New Ceramics as Column Packing Material for High Performance Liquid Chromatography

Masahiro KAWAHARA, Hiroshi NAKAMURA and Terumi NAKAJIMA

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo 113

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Silica gel and its derivatives have been predominant column packing materials for modern liquid chromatography owing to their high resolution.¹ However, their use is limited to the pH range 2.5 to 7.5 due to the chemical instability of their silica gel matrixes.² Nowadays, various type of new materials, *i.e.*, new ceramics, are easily available and their beneficial characteristics are widely known.³ On account of their ability to resist chemicals, heat and physical shocks, these new ceramics have been used as key materials for various devices in industries. On the other hand, the characteristics of these new materials indicate they should be usable as promising packing materials for high performance liquid chromatography (HPLC) as well. Therefore, we evaluated the adsorptive properties of some new ceramics, as a column packing material for HPLC, by using a newly developed method.

Experimental

Materials

Reagents and solvents were of guaranteed grade. Silica gel 60 for column chromatography (particle size, 0.063–0.200 mm), LiChrosorb Si-60 (5 μ m), and aluminum oxide 90 active neutral for column chromatography (0.063–0.200 mm) were purchased from E. Merck (Darmstadt, West Germany). Wakogel C-200 (0.074–0.149 mm) and zirconium silicate were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Zirconium nitride (1.35 μ m) and zirconium carbide (0.97 μ m) were kindly donated from Japan New Metals Co. Ltd. (Osaka, Japan); titanium oxide (1–2 μ m), zirconium oxide (3 μ m) and zirconium oxyphosphate were purchased from Soekawa Chemical Co., Ltd. (Tokyo, Japan).

Measurement of adsorption isotherms

The determination of the adsorption isotherms was carried out as follows. Twenty mg of the adsorbent was placed in individual test tubes and dried at 105°C for

2 h. A series of *p*-hydroxybenzoic acid (*p*-HBA) solutions of various concentrations were prepared with hexane-2-propanol (9:1). To each test tube containing the adsorbent, 500 μ l of each solution of *p*-HBA was added. After ultrasonication, the tubes were shaken rapidly at 40°C for 1 h. Thereafter the slurry was centrifuged, and the concentration of *p*-HBA in the supernatant (C_m ; μ M) was measured by the following reversed-phase HPLC.

HPLC

A TRIROTAR-VI (JASCO, Tokyo, Japan) HPLC system was used. *p*-HBA was separated on a TSK gel ODS-80T_M column (4.6 mm i.d. $\times$ 150 mm, 5 μ m, Tosoh, Tokyo, Japan) with isocratic elution using 0.02% HCl-acetonitrile (1:4) and detected at 254 nm.

Results and Discussion

There are several methods for testing performance of adsorbents; the shake-flask method⁴ is rapid and easy to control conditions, while it requires no special apparatus. Therefore, the adsorption isotherms were determined for *p*-HBA in hexane-2-propanol (9:1) on various new ceramics using the shake-flask method.

The amount of *p*-HBA adsorbed per weight of the adsorbent (C_s ; nmol/mg) was calculated from the following relationship

$$C_s = (C_0 - C_m) \times V / W \quad (1)$$

where C_0 (μ M) is the initial concentration of *p*-HBA, C_m (μ M) is the concentration of *p*-HBA in the supernatant, V (ml) is the volume of the solution, and W (mg) is the weight of the adsorbent. Figure 1 shows typical adsorption isotherms on silica gel (LiChrosorb Si-60), aluminum oxide, zirconium oxide and titanium oxide.

To represent the adsorption isotherms in liquid phase either Henry equation, Langmuir equation or Freundlich

equation is commonly used.^{5,6} The Henry equation (Eq. (2)) fits best for dilute solutions:

$$C_s = K_d \times C_m \quad (2)$$

The parameter K_d (l/g) is a distribution constant. The Langmuir equation (Eq. (3)) incorporates the assumptions of monolayer adsorption and uniformity of adsorption sites:

$$C_s = A \times Q_m \times C_m / (1 + A \times C_m) \quad (3)$$

A and Q_m (nmol/mg) represent the affinity and a maximum capacity of the adsorbent. To determine the

adsorption parameters, two linearized forms (Eq. (3a), (3b)) of the Langmuir equation are employed:

$$C_m / C_s = (1 / Q_m) \times C_m + 1 / (A \times Q_m) \quad (3a)$$

$$1 / C_s = (1 / A) \times (1 / Q_m) \times (1 / C_m) + 1 / Q_m \quad (3b)$$

The Freundlich equation (Eq. (4)) is an empirical equation:

$$C_s = K \times C_m^{1/n} \quad (4)$$

The parameter K is an adsorption capacity when $C_m=1$. The parameter n is related to the adsorption activity. The adsorption becomes firmer as n increases. Generally the adsorbents with n values of 2–5 are used.

Fig. 1 Adsorption isotherms on inorganic oxides: (▲) aluminum oxide; (□) zirconium oxide; (★) titanium oxide; (●) silica gel (LiChrosorb Si-60, 5 μm).

Fig. 2 Adsorption isotherms plotted on log-log graph: (▲) aluminum oxide; (□) zirconium oxide; (●) LiChrosorb Si-60; (★) titanium oxide; (Δ) Silica gel Si-60; (○) Wakogel C-200. Solid lines represent those by the Freundlich equation for each adsorbent.

Table 1 Summary of isotherm equation parameters

Adsorbent	Henry (Eq. (2))		Langmuir (Eq. (3a))			Langmuir (Eq. (3b))			Freundlich (Eq. (4))		
	$K_d / \text{l g}^{-1}$	r	A	$Q_m / \text{nmol mg}^{-1}$	r	A	$Q_m / \text{nmol mg}^{-1}$	r	K	n	r
Wakogel C-200	3.50×10^{-2}	0.980	2.11×10^{-2}	8.45×10^{-1}	0.974	4.64×10^{-3}	2.17	0.830	3.29×10^{-2}	1.61	0.985
Silica gel 60	9.43×10^{-3}	0.950	8.48×10^{-2}	1.96	0.957	7.66×10^{-3}	8.04	0.979	1.73×10^{-1}	1.72	0.968
LiChrosorb Si-60	7.77×10^{-3}	0.874	3.62×10^{-2}	8.89	0.986	1.18×10^{-2}	8.04	0.996	5.67×10^{-1}	2.16	0.980
TiO ₂	3.45×10^{-3}	0.892	2.40×10^{-2}	4.83	0.987	7.09×10^{-3}	7.40	0.991	3.56×10^{-1}	2.38	0.976
Al ₂ O ₃ Active 90	1.04×10^{-1}	0.953	1.48×10^{-3}	295	0.956	1.47×10^{-3}	284	0.975	1.78	1.52	0.973
ZrO ₂	5.17×10^{-2}	0.926	8.57×10^{-1}	50.8	0.856	1.26×10^{-2}	90.6	0.989	15.0	4.14	0.997
ZrSiO ₄	3.51×10^{-2}	0.936	9.21×10^{-1}	4.43	0.948	6.69×10^{-3}	8.32	0.962	1.66	3.48	0.974
ZrO·(H ₂ PO ₄)	6.29×10^{-3}	0.959	1.89×10^{-3}	7.23	0.989	3.65×10^{-3}	4.46	0.916	2.52×10^{-2}	1.23	0.974
ZrN	9.52×10^{-3}	0.959	3.10×10^{-2}	4.72	0.919	1.03×10^{-2}	8.18	0.977	3.13×10^{-1}	2.00	0.971
ZrC	1.65×10^{-2}	0.951	8.30×10^{-2}	1.99	0.864	5.43×10^{-3}	10.6	0.743	1.71×10^{-1}	1.61	0.964

Equation (5) is derived from the logarithmic transformation of Eq. (4) and predicts logarithmic proportionality between C_s and C_m :

$$\log C_s = (1/n) \log C_m + \log K. \quad (5)$$

The best-fit estimates of parameters and correlation coefficients of determination (r) were calculated and compared with each adsorbent (Table 1). Although the two Langmuir equations gave better r values than those obtained by the Henry equation, they showed rather poor representations over a wide range of solvent concentration. Equation (3a) fitted when C_m was high, while Eq. (3b) fitted when C_m was low. The Freundlich equation consistently gave good r values close to unity. The typical log-log plots between C_s and C_m obtained with some adsorbents are shown in Fig. 2.

Thus the adsorption isotherms on various adsorbents were found to be well represented by the Freundlich equation. These adsorption capacities were usable for the evaluation of the new ceramics as a column packing material for HPLC. These findings clearly show that the method presented here will be useful in choosing a column packing material for use in HPLC. Detailed

investigations will be reported elsewhere in the near future.

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