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Short communication

Preparation of monodisperse agglomerated pellicular anion-exchange resins compatible with high-performance liquid chromatography solvents for ion chromatography

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Abstract

Monodisperse agglomerated pellicular anion-exchange resins for high-performance ion chromatography are described. The resins are stable from pH 0 to 14 and from 1 to 100% (v/v) of common reversed-phase solvents in aqueous mixtures. © 1998 Elsevier Science B.V.

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1. Introduction

Since its introduction in 1975 by Small et al. [1], ion chromatography has become the dominant analytical method for determining inorganic anions (and some organic anions) at ppm–ppb level. However, for a long time, ion chromatography usually was used for the analysis of neat water samples, such as rain, river and drinking water. For the analysis of polluted water containing various organic compounds, rigorous pretreatment of the sample is necessary, otherwise the chromatographic column would be contaminated by the organic compounds. Although these compounds can be cleaned up with HPLC solvents, the column bed of polymer stationary phase could be damaged. An aqueous solution

containing more than 10% methanol will cause substantial change of the column bed. This drawback restricted the column lifetimes and the development of applied fields of the technique. Since 1990, Dionex has been successfully preparing columns for ion chromatography compatible with HPLC solvents through increasing degree of cross-linking of the polymeric substrate in the stationary phase [2]. With the new technique, treatment of the column using a typical eluent for reversed-phase LC, such as methanol or acetonitrile, can remove the organic contaminants easily. However, the polymer particle substrate used in the agglomerated pellicular stationary phase is not monodisperse and a broad particle size distribution is reported [3] to be disadvantageous as regards packing efficiency, flow conditions and operating pressure in the column. It is to be expected that an optimal packing may be obtained with

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monodisperse polymer particles. Here, we would like to report the preparation and properties of agglomerated pellicular anion exchangers using a monodisperse and highly cross-linked 10- μm polymer particle substrate.

2. Experimental

2.1. Apparatus

The chromatographic system consisted of a 5500 pump (Varian VISTA), a conductivity detector (Ionchrome 100), a micromembrane suppressor (851AMMS) and a Spectra-Physics SP 4400 integrator.

2.2. Reagents and materials

All eluents were made from HPLC grade solvents and other reagents were reagent-grade chemicals. Styrene monomer and divinylbenzene were imported from Dow. Styrene is 99% pure and inhibited by 10–15 ppm 4-*tert.*-butylcatechol (4-TBC). Divinylbenzene consists of a mixture of 55% *meta* and *para* isomers, 42% ethyl vinylbenzene, and 3% diethylbenzene, which is inhibited with ca. 1000 ppm 4-TBC. Styrene and divinylbenzene were stored at 5°C. The monomer and cross-linker were washed four times with an equal volume of an aqueous solution of 10% sodium hydroxide, followed by deionized water four times, in order to remove the inhibitor. Poly(vinyl alcohol) (PVA; DP 1700, degree of alcoholysis, 88%) was made at the Beijing Organic Chemicals Company (China).

The column capacity was determined by use of a breakthrough experiment. After the materials were packed into a stainless steel tube, 250 \times 4 mm I.D., the anion-exchange sites were converted to the OH-form. Each column was washed with deionized water until the effluent was neutral, and then it was connected to the conductivity detector. A solution of 0.0005 M hydrochloric acid was pumped through the column at 1 ml/min until breakthrough occurred.

For testing the columns, a mixture of 2.8 mM NaHCO₃ and 2.2 mM Na₂CO₃ was used as the eluent with a flow-rate of 2 ml/min, and a 0.025 mol/l sulfuric acid solution was used as the regener-

ant with a flow-rate of 138 ml/h; injection amount was 100 μl . The analytical columns prepared here were evaluated by their ability to separate an injection of seven anions obtained from reagent-grade salts in deionized water: 2.5 ppm F⁻, 3.5 ppm Cl⁻, 8.0 ppm NO₂⁻, 20 ppm PO₄³⁻, 10 ppm Br⁻, 10 ppm NO₃⁻, and 20 ppm SO₄²⁻. The HPLC solvent-compatible properties were tested with methanol as the eluent.

2.3. Substrate

The polymer particle substrate for this investigation was prepared with two-step swelling method developed by Ugelstag et al. [3–5]. Thus, monodisperse polystyrene seed particles (ca. 0.5 μm) were prepared by emulsion polymerization of styrene in water in the absence of emulsifier under a nitrogen atmosphere using potassium persulfate as the initiator according to the method reported by Zou et al. [6]. Then the seed particles were swollen with dioctyladipate, a highly water-insoluble compound of relatively low molecular mass. To facilitate the transport of the highly water-insoluble compound through the aqueous phase to become absorbed into the particles, dioctyladipate may be added in the form of an emulsion. In addition, one may add to the system a solvent which is miscible with water and is a solvent for dioctyladipate. In this way we produced particles containing dioctyladipate in a v/v ratio of 1:2 with respect to polymer. Then water, 55% divinylbenzene, initiator and emulsifier (PVA) were added, and the activated seeds allowed to swell with monomer to 5, 10 and 30 μm or more. After completion of the swelling, the temperature is raised and the polymerization carried out.

2.4. Ion-exchange latex

The ion-exchange latex used in this work was synthesized by copolymerization of 5% divinylbenzene with 95% vinylbenzyl chloride using emulsion polymerization techniques according to the method reported by Chong [7] and then quaternized with dimethylethanolamine. The sizes of latexes before and after functionalization are 60 and 95 nm, respectively. As can be seen from these data, functionaliza-

tion increases the diameter of the 5% cross-linked latexes by about 60%.

2.5. Agglomerated pellicular anion-exchange resins

The highly cross-linked monodisperse particles of 10 μm were sulfonated to 6 $\mu\text{equiv./g}$ using sulfuric acid, then the surface-sulfonated particles and the above ion-exchange latex were mixed for 3 h, the excess of emulsion was removed and the agglomerated pellicular stationary phase for ion chromatography was obtained. The exchange capacity of this stationary phase was about 20 $\mu\text{equiv./g}$. Pressure packing at 3000 p.s.i. (1 p.s.i.=6894.76 Pa) using stainless steel columns (250 \times 4.0 mm) and Valco end fittings (Valco Instruments) was carried out by the slurry method. The column ion-exchange capacity was about 60 $\mu\text{equiv.}$

3. Results and discussion

Most of the ion chromatography columns in use today are electrostatically latex-coated pellicular ion exchangers. These materials consist of three regions: (1) an inert polystyrene–divinylbenzene (PS–DVB) core, (2) a shallow sulfonated layer on the surface of the inert core, (3) a mono-layer coating of colloidal ion-exchange particles which are permanently attached to the oppositely charged, functionalized surface of the inert core. The latex coating consists of fully functionalized anion-exchange latex particles made from vinylbenzylchloride (VBC) polymer cross-linked with DVB and fully functionalized with an appropriate tertiary amine for desired anion-exchange selectivity [8,9].

Study shows that column capacity is influenced by the particle sizes of the latexes and substrate, and efficiency is most strongly effected by size of the substrate resin [8].

By the method previously described, porous and nonporous monodisperse particles of 3–50 μm with different degrees of cross-linking can be obtained. For the preparation of HPLC solvent-compatible stationary phase for ion chromatography, 55% divinylbenzene was used as the monomer and highly cross-linked, monodisperse particles of 10 μm , with standard deviation of $<0.2 \mu\text{m}$, were obtained. Figs.

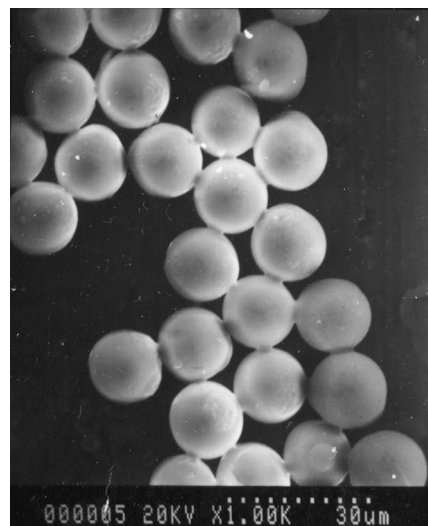


Fig. 1. SEM of DVB particles.

1 and 2 are photographs taken by scanning electron microscopy (SEM) showing unagglomerated 10- μm sulfonated monodisperse divinylbenzene substrate resin at 1000 \times magnification, and substrate agglomerated with 0.1- μm latex at 10000 \times magnification, respectively. Seven anions were baseline separated

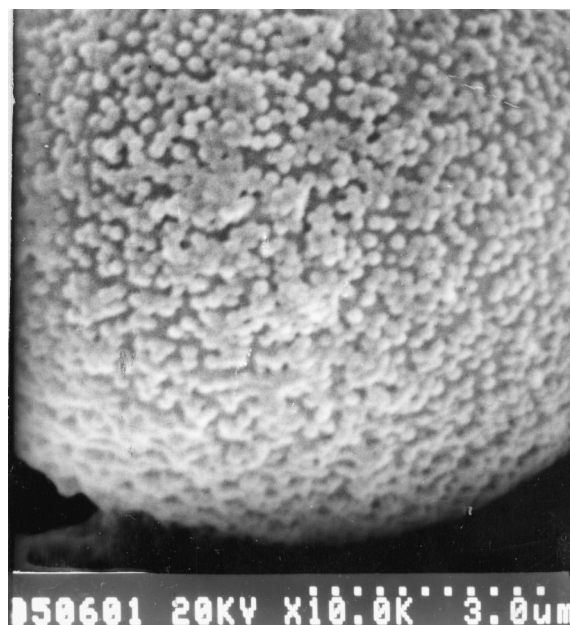


Fig. 2. SEM of the agglomerated pellicular resin.

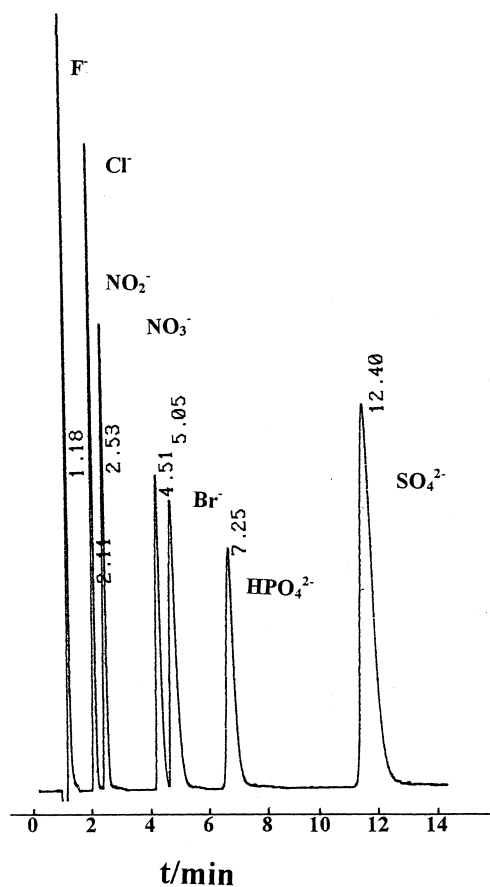


Fig. 3. Separation of anions using agglomerated resin as the packing.

on the column (Fig. 3). The retention time, resolution and column efficiency are given in Table 1 and these are comparable with the product Dionex-AS4A-SC. Penetration and solvent-compatible properties were tested with methanol as the eluent. After

elution for 20 min the column pressure decreased from the starting 647 to 521 p.s.i., and the latter value was stable during further elution. After 3 h, the column was eluted with the standard elution, the column pressure was recovered and was stable at 648 p.s.i. Retest of the separation of the anions gave a result exactly the same as that before the elution with methanol, indicating no damage to the column. It was noted that the low column pressure revealed a much better penetration because of the monodispersibility, and this is favorable for column lifetime and practical operation. The reproducibility of retention time and peak height in the tests were excellent. The linearity between ion concentration and peak height was studied through dilution of the standard solutions of 2, 4, 6, 8, and 9 ml to 10 ml. Calculation with the linear normalization equation ($y=a+bx$) gave correlation coefficients 0.996–0.999.

In summary we have successfully prepared an HPLC solvent-compatible, monodisperse agglomerated pellicular anion exchanger for ion chromatography.

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Table 1
Separation, retention times and column efficiency

	Anion						
	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	HPO ₄ ²⁻	SO ₄ ²⁻
Concentration (ppm)	2.5	3.5	8.0	10	10	20	20
Retention times (min)	1.18	2.13	2.55	4.61	5.17	7.18	12.25
Resolution (R_s)		6.13	2.40	8.53	1.60	6.28	7.55
Efficiency (plates/m)	7084	18 864	9955	13 460	8760	13 124	13 572

Efficiency was calculated by $N=5.54(t_R/w_{1/2})^2$, where t_R and $w_{1/2}$ are the retention time and the width at half height for the corresponding ions.

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