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Study of ion chromatography with ion-exchange fibers as the stationary phase

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Abstract

The application of ion-exchange fibers as the stationary phase in ion chromatography for the separation of inorganic anions has been studied. Results indicate that a separator column packed with VS-2 anion-exchange fibers and a suppressor column packed with VS-1 cation-exchange fibers have a similar separation efficiency to small-particle resin columns, but that the column pressure drop (ΔP) in fiber columns is only one-tenth of that in resin columns, at the same flow-rate. This allows the separation to be performed efficiently at a higher flow-rate and with lower pressure, as shown for the separation of an anion mixture.

Keywords: Stationary phases, LC; Ion-exchange fibers; Inorganic anions

1. Introduction

Since its introduction by Small et al. [1] in 1975, ion chromatography (IC) has become a rapid, accurate and sensitive chromatographic method for the separation and determination of inorganic and organic anions [2–4]. Many studies on new packing materials and new detection techniques have been reported [5,6]. However, a disadvantage of conventional small-particle resin (SPR) packings in IC is that high pressure is required for an adequate mobile phase flow. Ion-exchange fibers (IFs), a type of functional material developed early in 1950 [7], have some special features such as large surface area, high exchange rate and low exchange capacity. These

special features can meet the requirement for low-pressure and high-performance IC. Some approaches have been described for the application of hollow IFs in packing suppressor columns [8–11]. No information is available on using solid IFs as the stationary phases for both the separator and suppressor columns in IC. We became interested in filling this gap using two types of solid IFs, VS-1 and VS-2, as packings. VS-1 and VS-2 are both partially dehydrated poly(vinyl alcohol) (PVA)-based, and are derivatized with sulfonic acid groups and quaternary ammonium groups, respectively. This paper describes an investigation of the performance of a separator column packed with VS-2 anion-exchange fibers and a suppressor column packed with VS-1 cation-exchange fibers for the separation of inorganic anions.

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2. Experimental

2.1. Materials and reagents

VS-1 and VS-2 IFs were supplied by Liaoyuan Science and Technology Institute (Liaoyuan, China). Both have a fiber diameter of 36 μm . The exchange capacity of VS-1 is 0.71 mmol/g H^+ and that of VS-2 is 0.08 mmol/g CO_3^{2-} . YSG- SO_3H and YSG- $\text{RN}^+(\text{CH}_3)_3\text{Cl}^-$ resins have a diameter of 15–20 μm . Eluents and standard solutions of anions were prepared by dissolving analytical-reagent-grade salts in freshly deionized water, and the eluents were filtered through a 0.5- μm membrane filter before use.

2.2. Instrumentation

A Model SY-221 ion chromatograph was used with a DDJ-01 conductivity detector (Ninth Meter Factor, Schuan, China), equipped with a Model YSB-2 constant-flow pump (Shanghai Academy of Science, Shanghai, China). A 250 \times 3.0 mm I.D. IC stainless-steel column, packed with VS-1 H^+ cation-exchange fibers ($d=36 \mu\text{m}$, $L=1 \text{ mm}$), was used as the suppressor column. A 250 \times 1.8 mm I.D. IC glass column packed with VS-2 CO_3^{2-} anion-exchange fibers ($d=36 \mu\text{m}$, $L=1 \text{ mm}$) was used as the separator column. The packing density of IFs in both columns was 0.165 g/ml. In order to allow a comparison of the pressure drop (ΔP) characteristics and the separation efficiency with an SPR column system, a suppressor column (250 \times 5 mm I.D. IC glass column) was packed with high-capacity YSG- SO_3H resin and a separator column (250 \times 3 mm I.D. IC glass column) was packed with YSG- RN^+ -

$(\text{CH}_3)_3\text{Cl}^-$ low-capacity resin using conventional slurry packing.

2.3. Procedure

IFs were cut to lengths (L) of 1 mm, soaked in deionized water for 24 h and packed into columns using the layering wet-packed method. The columns were eluted with 1.0 mol/l NaOH, 1.0 mol/l HNO_3 and deionized water. The separator column was converted to a CO_3^{2-} exchanger with 0.0024 mol/l Na_2CO_3 and the suppressor column was converted to a H^+ exchanger with 1.0 mol/l HNO_3 before being connected to an ion chromatograph. Columns were then eluted with 0.0024 mol/l Na_2CO_3 , until the value of conductivity cell was below 20 μS . The same procedure was used for a SPR column system. All experiments were performed at room temperature.

3. Results and discussion

3.1. Comparison of column pressure drops between IF and SPR columns

The experimentally obtained pressure drop characteristics of the fiber column system are shown in Table 1. It is immediately evident that the fiber columns exhibit a substantially lower pressure drop, with a pressure drop of no more than one-tenth of that in the SPR columns at the same flow-rate. These data show that it will be possible to operate the fiber column system at an elevated flow-rate, while maintaining an acceptable pressure drop. IC with such low pressure drops can decrease the problems of

Table 1
Comparison of ΔP between IF columns and SPR columns

| Number | Flow-rate (ml/min) | SPR columns | | IF columns | |
|--------|-----------------------|---------------------------|--------------------|---------------------------|--------------------|
| | | Linear velocity (mm/s) | ΔP (Pa) | Linear velocity (mm/s) | ΔP (Pa) |
| 1 | 0.5 | 1.17 | 8.0×10^5 | 3.33 | 6.0×10^4 |
| 2 | 1.0 | 2.35 | 1.7×10^6 | 6.67 | 1.0×10^5 |
| 3 | 2.0 | 4.69 | 3.4×10^6 | 13.5 | 2.0×10^5 |
| 4 | 3.0 | 7.03 | 4.9×10^6 | 20.0 | 3.0×10^5 |

leakage and blockage, etc., and result in high performance.

3.2. Effect of eluent flow-rates on retention time and separation efficiency

Experiments were attempted using F^- and Cl^- as the sample ions in our fiber column system. Results in Fig. 1 show that the retention times of Cl^- reduce and the peaks narrow with increasing flow-rate of the eluent. This is because ion-exchange fibers have the advantages of low capacity, excellent dynamic performance and rapid mass-transfer ability, as found in our previous study [12]. Fig. 2 shows the separation of F^- and Cl^- in a standard anion mixture. With regard to the resolution between F^- and Cl^- , a decrease is observed with increasing flow-rate of the eluent. However, it is clear that F^- and Cl^- can be separated on the fiber columns at a flow-rate of below 3 ml/min. The efficiency of separation is reported as HETP (H), calculated by the half-height method ($H=L/5.54(t_R/w_{1/2})^2$). A plot of H versus velocity (u) for F^- and Cl^- on the fiber columns is shown in Fig. 3. The H versus u plots increase gradually with increasing velocity, showing a decrease in column efficiency when the flow-rate of the eluent is increased considerably.

3.3. Effect of eluent concentration on the separation efficiency

Fig. 4 shows that the retention times of F^- and Cl^- reduce and the peaks narrow with increasing eluent concentration, whereas the resolution between F^- and Cl^- increases. Taking into consideration that the useful lifetime of the suppressor column is decreased by high concentrations, an eluent concentration of 0.0024 mol/l may be better.

3.4. Calibration of the experimental method

Calibration graphs were obtained by plotting peak heights against the concentration of F^- , Cl^- , NO_2^- and NO_3^- , and by plotting peak areas against the concentrations of PO_4^{3-} and SO_4^{2-} . Linear calibration graphs were in the following ranges for the anions: F^- , 0–5 $\mu g/ml$; Cl^- , 0–5 $\mu g/ml$; NO_2^- , 0–9 $\mu g/l$

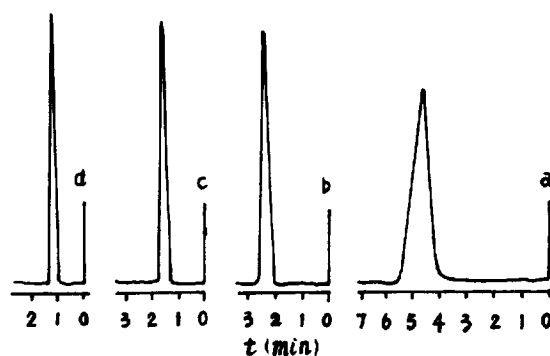


Fig. 1. Effect of eluent flow-rates on retention time. Peaks: Cl^- (3 $\mu g/ml$); flow-rates: a=1, b=2, c=3 and d=4 ml/min; eluent: 0.0024 mol/l Na_2CO_3 .

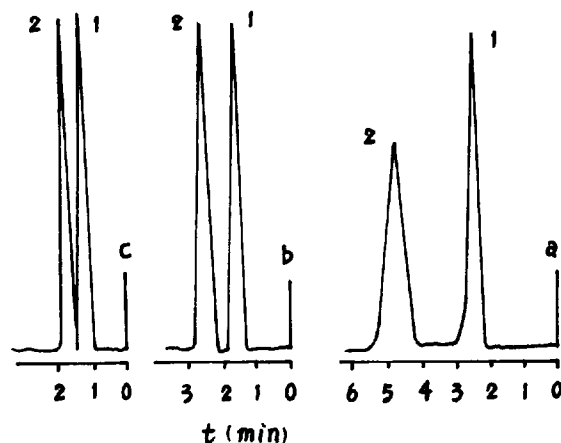


Fig. 2. Effect of eluent flow-rates on the efficiency of separation. Peaks: 1= F^- (2 $\mu g/ml$); 2= Cl^- (3 $\mu g/ml$); eluent, 0.0024 mol/l Na_2CO_3 ; flow-rates: a=1 ml/min; b=2 ml/min; c=3 ml/min.

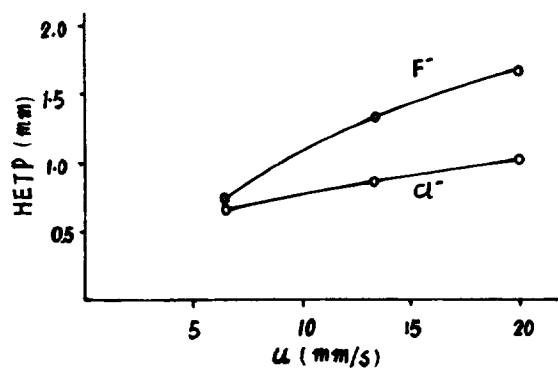


Fig. 3. H versus u plots for the IF columns.

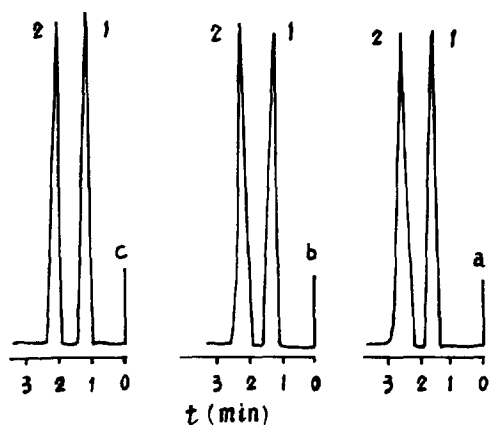


Fig. 4. Effect of the concentration of eluent on the efficiency of separation. Peaks: 1= F^- ($2 \mu\text{g/ml}$), 2= Cl^- ($3 \mu\text{g/ml}$); flow-rate of eluent, 2 ml/min. Concentration of eluent, a=0.0024 mol/l; b=0.0036 mol/l; c=0.0048 mol/l.

ml; NO_3^- , 0–25 $\mu\text{g/ml}$; PO_4^{3-} , 0–60 $\mu\text{g/ml}$ and SO_4^{2-} , 0–80 $\mu\text{g/ml}$.

The precision and repeatability were assessed by performing five replicate analyses of every standard solution. The standard solutions with different concentrations were prepared by successive dilutions. The results shown in Table 2 indicate that the method is capable of good precision; the good chromatographic peak profiles together with the steady baseline obtained by the method contribute to

Table 2
Determination of anions in standard solutions

| Anion | Added ($\mu\text{g/ml}$) | Found ($\mu\text{g/ml} \pm \text{S.D.}, n=5$) | Recovery (%) | R.S.D. (%) |
|----------|-------------------------------|--|-----------------|---------------|
| F^- | 1.50 | 1.50 ± 0.005 | 100.0 | 0.33 |
| | 2.50 | 2.45 ± 0.051 | 98.0 | 2.04 |
| | 3.50 | 3.52 ± 0.037 | 100.6 | 1.06 |
| Cl^- | 1.50 | 1.48 ± 0.052 | 98.6 | 3.47 |
| | 2.50 | 2.47 ± 0.034 | 98.8 | 1.36 |
| | 3.50 | 3.50 ± 0.041 | 100.0 | 1.17 |
| NO_2^- | 2.00 | 2.04 ± 0.09 | 102.0 | 4.50 |
| | 4.00 | 4.05 ± 0.10 | 101.3 | 2.50 |
| | 6.00 | 6.04 ± 0.12 | 101.0 | 2.00 |
| NO_3^- | 5.0 | 5.05 ± 0.10 | 101.0 | 2.00 |
| | 10.0 | 10.02 ± 0.15 | 100.2 | 1.50 |
| | 15.0 | 14.96 ± 0.13 | 99.7 | 0.86 |

Eluent: 0.0024 mol/l Na_2CO_3
Flow-rate: 2.0 ml/min.

this good repeatability. It is clear that IC with IFs as packings can be used for quantitative analysis.

3.5. Separation of a standard anion mixture

To illustrate the practical utility of the IF column system, we present, as an example, the separation of a mixture of F^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-} in Fig. 5a. All anions can be separated as sharp and

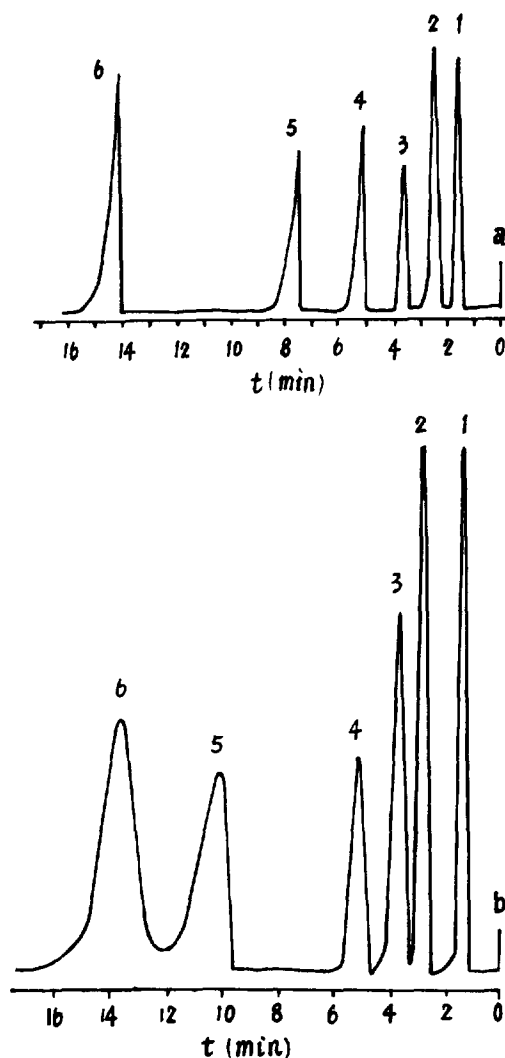


Fig. 5. Chromatograms of a standard anion mixture, (a) on the IF columns, (b) on the SPR columns. Eluent, 0.0024 mol/l Na_2CO_3 . Flow-rate, 2 ml/min. Peaks: 1= F^- ($2 \mu\text{g/ml}$); 2= Cl^- ($3 \mu\text{g/ml}$); 3= NO_2^- ($6 \mu\text{g/ml}$); 4= PO_4^{3-} ($10 \mu\text{g/ml}$); 5= NO_3^- ($20 \mu\text{g/ml}$); 6= SO_4^{2-} ($40 \mu\text{g/ml}$).

symmetrical peaks, and the baseline drift and noise are very low. This result is derived from the high permeability of solid IFs, as determined in our previous investigation [12]. IFs used in both separator column and suppressor column have an exchange layer of 4.3 μm [which is shorter than those required for SPR ($d=25 \mu\text{m}$)] and the time needed for reaching exchange equilibrium is about 50 s. These two advantages endow IFs with a rapid mass-transfer ability. It can be seen that there is a great decrease in band broadening and an increase in resolution, when Fig. 5a is compared with Fig. 5b.

4. Conclusions

The potential of using IFs as packing materials in IC for the separation of inorganic anions has been satisfactorily investigated. The column pressure drop exhibited on IF columns is only one-tenth of that on SPR columns at the same flow-rate. A higher efficiency of separation can be achieved at a lower column pressure drop in comparison with the SPR columns. The precision and repeatability of determinations are excellent and the method is suitable for quantitative analysis. It is suggested that IFs not only can be used efficiently as packings in IC for the

separation of inorganic anions, but also represent a new concept for choosing stationary phase in IC.

References

- [1] H. Small, T.S. Steens and W.C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- [2] O.A. Shpigun and Yu.A. Zolovov, *Ion Chromatography in Water Analysis*, Ellis Horwood, Chichester, 1988.
- [3] W.T. Frankerberger, H.C. Mehra and G.T. Gjerde, *J. Chromatogr.*, 504 (1990) 53.
- [4] C.F. Pereira, *J. Chromatogr.*, 624 (1992) 457.
- [5] J.G. Tarter, in J.G. Tarter (Editor), *Ion Chromatography* (Chromatographic Science Series, Vol. 37), Marcel Dekker, New York, 1987, Ch. 7, p. 369.
- [6] H. Small, *Ion Chromatography*, Plenum Press, New York, 1989.
- [7] A.D. Virnik, L.S. Galbraikh and R.M. Livshits, *Zh. V ses. Kyim. Obschest*, 11 (1966) 657.
- [8] Y. Hanaoka, T. Murayama, S. Muramoto, T. Matura and A. Nanba, *J. Chromatogr.*, 239 (1982) 537.
- [9] T.S. Stevens, J.C. Davis and H. Small, *Anal. Chem.*, 53 (1981) 1488.
- [10] P. Dasgupta, *Anal. Chem.*, 56 (1984) 103.
- [11] T.S. Stevens, G.L. Jewett and R.A. Bredeweg, *Anal. Chem.*, 54 (1982) 1206.
- [12] L.Q. Chen, G.L. Yang and Z. Zheng, *Acta Chim. Sinica* (China), 52 (1994) 116.