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Journal of Chromatography A, 845 (1999) 165–170

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Simultaneous separation of anions and cations by flow-gradient ion chromatography

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Abstract

A new method to allow the simultaneous separation of anions and cations is proposed. It uses both the anion- and cation-exchange column connected in series, and uses two pumps with a flow-gradient capability. Two eluents delivered by these two pumps are merged in between the two columns. By varying the flow rates of two pumps and keeping the total flow-rate constant, retention times of both anions and cations can be controlled so that they are well separated. This new method was applied to a simultaneous separation of monovalent cations and anions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Flow-gradient chromatography; Gradient elution; Inorganic anions; Inorganic cations

1. Introduction

Ion chromatography developed by Small et al. [1] in 1975 is now being recognized as a very powerful method for analysis of anions and cations in a variety of aqueous solutions. Many studies have centered on either cations or anions, while four methods for a simultaneous analysis of both ions have been so far proposed. The first is a method to use a complexing reaction to change metal cations to complex anions and then, separates them by using an anion-exchange column, together with anions in a sample [2,3]. The second method uses two anion- and cation-exchange columns connected in series [4–7] or uses a single ion-exchange column packed both anion- and cation-exchange resins [8]. These methods separate both anions and cations in a sample to some extent, by carefully choosing eluent. However, it is in general difficult to apply these methods to samples con-

taining many kinds of anions and cations. The third one is a method using the both anion and cation-exchange columns in series and combining a column-switching technique [9,10]. Even in this method, a column-switching timing has to be carefully adjusted to avoid peak overlaps in addition to a selection of proper eluent. The fourth method uses a single weakly acidic cation-exchange column to separate cations by ion-exchange and anions by ion exclusion [11]. And also, the similar method using a single ODS (octadecyl silica) column coated with weakly/strongly charged zwitterionic stationary phase was proposed [12,13]. These methods are simple, but the separation based on ion exclusion may be difficult to extend to many anions.

In this paper, we propose a new method to allow the simultaneous separation of anions and cations, which uses both the strong anion- and strong cation-exchange columns connected in series as well as the second type method [14]. It, however, requires two pumps with a flow gradient capability. Two eluents

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delivered by these pumps are merged in between the two columns. By varying the flow rates of two pumps and keeping the total flow-rate constant, retention times of both anions and cations can be controlled so that they are well separated. We will show in the following sections how this new method works and can be applied to monovalent cations and anions.

2. Experimental

2.1. Chemicals

Eluents were prepared by dissolving analytical-grade benzoic acid and tris(hydroxymethyl)aminomethane (Tris), with deionized water. The standard sample containing monovalent cations and anions was also prepared by dissolving analytical grade compounds with the deionized water. The concentration of each ion in this standard sample is as follows:

Cations (ppm)	Anions (ppm)
Li ⁺ : 8	Cl ⁻ : 79
Na ⁺ : 52	NO ²⁻ : 51
NH ⁴⁺ : 19	Br ⁻ : 89
K ⁺ : 42	NO ³⁻ : 65

2.2. Apparatus

Chromatography was performed on Hitachi ion chromatograph consisting of two L-7100 pumps, L-7200 autosampler, L-7300 column oven, L-7470 conductivity detector, and D-7000 chromatography data station, which can control these modules and generate reports. The separation columns used were Hitachi IC 2710 strong anion-exchange column (size: 50 mm×4.0 mm I.D., packed material: methacrylate polymer resin, diameter: 10 μm, ion-exchange capacity: 20 mequiv./g) and Hitachi IC 2720 strong cation-exchange column (size: 50 mm×4.0 mm I.D., packed material: styrene-divinylbenzene co-polymer resin, diameter: 10 μm, ion-exchange capacity: 20 mequiv./g). Fig. 1 schematically shows a flow diagram of the simultaneous analysis system of cations and anions, which is called here flow-gradient ion chromatography (IC). The both column

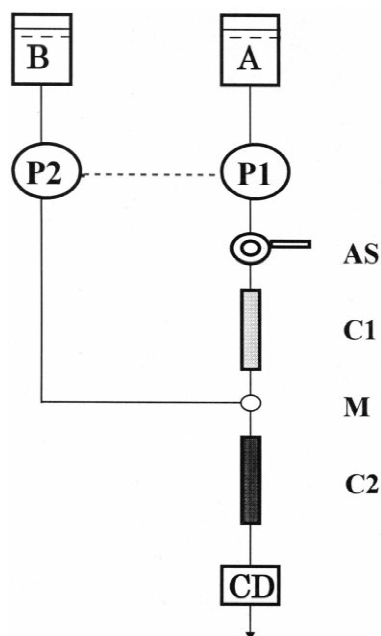


Fig. 1. Flow diagram of flow-gradient ion chromatography system A and B: Eluent (A=B), P1 and P2: Pumps with high-pressure gradient capability, AS: Autosampler, C1 and C2: cation(anion)-exchange and anion(cation)-exchange columns, M: Mixer (or T-joint), CD: Conductivity detector.

orders, i.e., (1) cation-exchange column and anion-exchange column, and (2) vice versa, were tested.

The analytical conditions were as follows. The two columns and the flow cell of conductivity detector were installed in the column oven and the temperature was always maintained at 40°C. A polarity of conductivity detector was set to 'positive'. The both pumps were controlled by binary high-pressure gradient mode so that a sum of the both flow rates is kept constant, e.g., 1.0 ml/min. An injection volume of the standard sample was usually 10 μl.

3. Result and discussion

Before starting the simultaneous analysis of both ions, we tested several eluents varying the concentrations of benzoic acid and Tris and using the single (cation-exchange or anion-exchange) column. As Fig. 2 shows, the eluent (2.5 mM benzoic acid and 1.5 mM Tris) was reasonable for the separation

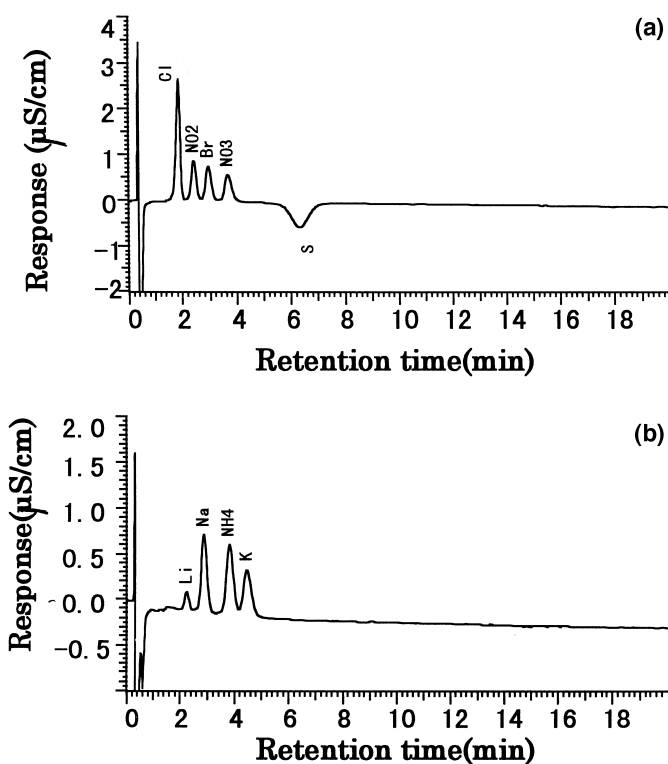


Fig. 2. (a) Anions separated by anion-exchange single column $P1=1.0$ ml/min ($P2$: not used). Eluent A: 2.5 mM benzoic acid+ 1.5 mM Tris. Analytes: the standard sample (S: system peak). Injection volume: 10 μ l. Column: Hitachi IC 2710(50 mm \times 4.0 mm I.D.). (b) Cations separated by cation-exchange single column $P1=1.0$ ml/min ($P2$: not used). Eluent A: 2.5 mM benzoic acid+ 1.5 mM Tris. Analytes: the standard sample. Injection volume: 10 μ l. Column: Hitachi IC 2720(50 mm \times 4.0 mm I.D.).

of the monovalent cations and anions in this single column system, respectively. So, it was always used for both eluents A and B for the simultaneous analysis of cations and anions by the flow-gradient IC.

First, the flow-gradient IC using the cation-exchange column and the anion-exchange column was tested. Fig. 3a is the chromatogram obtained by using only Pump 1($P1$), that is, $P1$'s flow rate is 1.0 ml/min and $P2$'s flow rate is 0.0 ml/min. In this chromatogram, only the first and last peaks are separated and identified as Cl^- and K^+ , respectively. It may be possible to obtain a better separation by carefully changing the eluent composition. If Pump 2 is used in this system, it is not so difficult to separate these cations and anions. In Fig. 3b, $P1$'s and $P2$'s flow rates were set to 0.2 ml/min and 0.8 ml/min, respectively, and a complete separation of the cations and the anions was achieved. However, the cation

peaks slowly eluted by the flow rate $P1=0.2$ ml/min become broad and as a result, an analysis time is about 3 times longer than that of Fig. 2b.

These problems can be partially solved by changing the flow rates during the elution. Here, it should be noted that after the anions are completely eluted, a role of $P2$ ends. Therefore, $P2$'s flow rate can be decreased to 0.0 ml/min suddenly or linearly after eluting the anions, while $P1$'s flow rate can be increased to 1.0 ml/min suddenly or linearly. As the sum of both flow rates is always kept 1.0 ml/min, this is the so-called high-pressure gradient elution and also, this is the reason why this method is called as the flow gradient IC in this paper in this paper. Fig. 3c is the chromatogram obtained by linearly changing the both pump flow rates between 7 and 17 min (see also the curves of $P1$'s and $P2$'s flow rate overlaid on chromatogram, which are corresponding to $P1$ and $P2$ flow rates, respectively). Thus, the peak

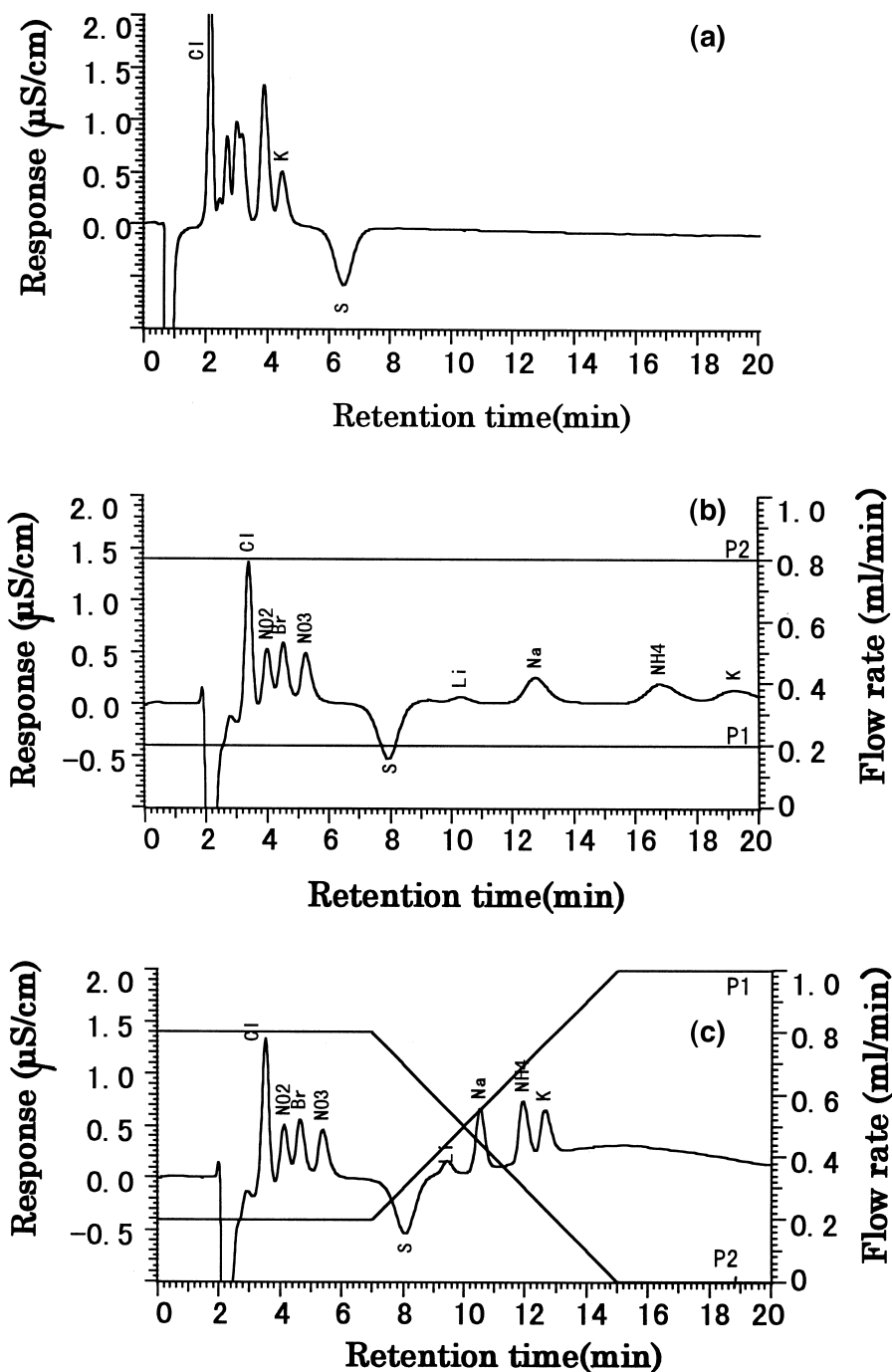


Fig. 3. (a) Anions and cations separated by the flow gradient IC system (cation-exchange column and anion-exchange column) P1=1.0 and P2=0.0 ml/min. Eluent A: 2.5 mM benzoic acid+1.5 mM Tris. Analytes: the standard sample (S: system peak). Injection volume: 10 μl . Columns: Hitachi IC 2720 (50 mm \times 4.0 mm I.D.) and Hitachi IC 2710 (50 mm \times 4.0 mm I.D.) (b) Anions and cations separated by the flow gradient IC system (cation-exchange column and anion-exchange column). Constant flow rates P1=0.2 and P2=0.8 ml/min as shown. Other chromatographic conditions as in Fig. 3a. (c) Anions and cations separated by the flow gradient IC system (cation-exchange column and anion-exchange column). Flow gradient of P1 and P2 as shown. Other chromatographic conditions as in Fig. 3a.

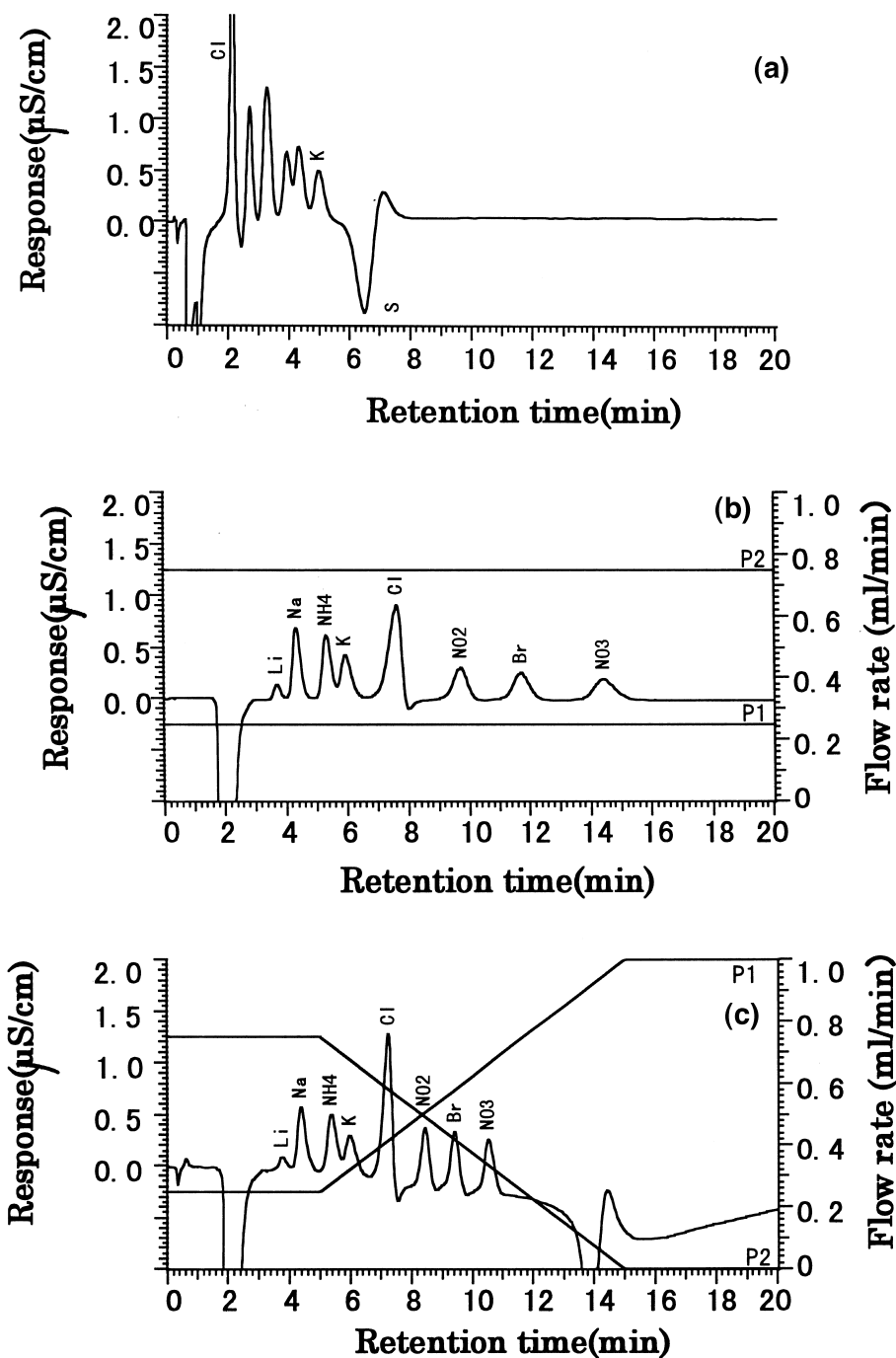


Fig. 4. (a) Anions and cations separated by the flow gradient IC system (anion-exchange column and cation-exchange column) P1=1.0 and P2=0.0 ml/min. Eluent A: 2.5 mM benzoic acid+1.5 mM Tris. Analytes: the standard sample (S: system peak). Injection volume: 10 μl . Columns: Hitachi IC 2710 (50 mm \times 4.0 mm I.D.) and Hitachi IC 2720 (50 mm \times 4.0 mm I.D.). (b) Anions and cations separated by the flow gradient IC system (anion-exchange column and cation-exchange column). Constant flow rate P1=0.25 and P2=0.75 ml/min as shown. Other chromatographic conditions as in Fig. 4a. (c) Anions and cations separated by the flow gradient IC system (anion-exchange column and cation-exchange column). Flow gradient of P1 and P2 as show. Other chromatographic conditions as in Fig. 4a.

Table 1
Repeatability of peak retention time (t_R) and peak area ($n=5$)
under the same condition as Fig. 3c

Ion	RSD (%)	
	t_R	Area
Cl ⁻	0.29	0.47
NO ²⁻	0.27	0.76
Br ⁻	0.25	0.58
NO ³⁻	0.23	1.60
Li ⁺	0.34	1.57
Na ⁺	0.17	1.61
NH ⁴⁺	0.14	0.13
K ⁺	0.13	0.68

shapes of cations are sharpened and their retention times are shortened. Due to the flow rate changes, the baseline slightly drifts despite that the eluent delivered by the pumps 1 and 2 is same, i.e., eluent A=B in Fig. 1.

Table 1 denotes a repeatability of each peak retention time (t_R) under the five injections. RSDs(%) (relative standard deviations) of all peak retention times are less than 0.34(Li⁺) and shows that the flow gradient in this system is stable. Table 1 also denotes a repeatability of each peak area. Except for Li⁺ influenced by the so called system peak (or, vacant dip) denoted by S in Fig. 3, the other ions show a good repeatability less than RSD=1.7%(Na⁺).

Fig. 4 shows the chromatograms obtained by the flow-gradient IC with the column order opposite to that of Fig. 3, that is, the anion-exchange column and the cation-exchange column. As well as Fig. 3a, Fig. 4a is the chromatogram obtained by using only Pump 1(P1), that is, P1's flow rate is 1.0 ml/min and P2's flow rate is 0.0 ml/min. In this case, most peaks overlap. Fig. 4b shows the chromatogram obtained by setting up the flow rates of P1=0.25 and P2=0.75 ml/min, respectively. Then, the cations and anions are completely separated. Here, it should be noted that the separation order of cations and anions are opposite to that of Fig. 3b because of the opposite order of the column connection. Fig. 4c is the chromatogram obtained by changing the flow rates of P1 and P2 as shown by the overlaid curves. Thus, an analysis time of both ions can be shortened. How-

ever, the peak shapes of the anions slightly deform in this case. We think that this deformation is due to a characteristics of the anion-exchange column packed methacrylate polymer resin under the high column pressure about 2.3 MPa, because the similar deform are not seen in Fig. 3b and Fig. 3c under the column pressure less than 1.5 MPa. In addition, the similar peak deformation does not happen in the cation-exchange column packed styrene-divinylbenzene copolymer resin which has a higher pressure resistance than the methacrylate polymer resin.

4. Conclusion

The flow-gradient IC method developed in this study is useful for a simultaneous separation of both anions and cations. When the same eluent is delivered by the both pumps, baseline drift of chromatogram can be minimized and as a result, a good repeatability of peak areas and retention times can be obtained. The eluent 2.5 mM benzoic acid and 1.5 mM Tris is suitable for the separation of these monovalent anions and cations.

References

- [1] H. Small, T.S. Stevens, W.C. Bauman, *Anal. Chem.* 47 (1975) 1801.
- [2] D.R. Jenke, G.K. Pagenkoph, *Anal. Chem.* 55 (1983) 1168.
- [3] M. Yamamoto, H. Yamamoto, Y. Yamamoto, S. Matsushita, N. Baba, T. Ikushige, *Anal. Chem.* 56 (1984) 832.
- [4] H. Small, T.E. Miller Jr., *Anal. Chem.* 54 (1982) 462.
- [5] Z. Ishandarani, T.E. Miller Jr., *Anal. Chem.* 57 (1985) 1591.
- [6] V.K. Jones, J.G. Tarter, *J. Chromatogr.* 312 (1984) 456.
- [7] V.K. Jones, S.A. Frost, J.G. Tarter, *J. Chromatogr. Sci.* 23 (1985) 442.
- [8] D.J. Pietrzyk, D.M. Brown, *Anal. Chem.* 58 (1986) 2554.
- [9] R. Saari-Nordhaus, J.M. Anderson Jr., *J. Chromatogr.* 549 (1991) 257.
- [10] R. Saari-Nordhaus, L. Nair, J.M. Anderson Jr., *J. Chromatogr.* 602 (1992) 127.
- [11] K. Tanaka, K. Ohta, J.S. Friz, S. Matsushita, A. Miyayaga, *J. Chromatogr. A* 671 (1994) 239.
- [12] W. Hu, H. Haraguchi, *Anal. Chem.* 66 (1994) 765.
- [13] W. Hu, A. Miyazaki, H. Haraguchi, *Anal. Sci.* 11 (1995) 999.
- [14] K. Deguchi and M. Ito, *Japan Pat.*, 1 987 534.