New approach for controlling the partitioning of analyte ions in ion chromatography with a water mobile phase

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Abstract

The problem of the "confusing" distribution of analyte ions in quantitative analysis using ion chromatography with a water mobile phase (water mobile-phase ion chromatography, WMP-IC) has been overcome. Hence, the number of possible applications of ion chromatography using water as the mobile phase is vastly enhanced. In previous WMP-IC studies of inorganic ions, each analyte cation and/or anion species was distributed to each counterion species and co-eluted as ion pairs. Such a partitioning of the analyte ions hampers their quantitative analysis because calibration graphs must be derived for all possible ion pairs. This paper deals with a simple and convenient method to obtain an "exclusive" partitioning, i.e. where each analyte ion species exists in only a single ion pair. This was achieved by the addition of specific ions to the sample solution to regulate the number of species and the concentration ratio of the ions in the sample solution. "Exclusive" partitioning of the analyte ions and their precise detection have been realized.

1. Introduction

The use of water as the mobile phase is the most desirable approach for further application and simplification of ion chromatography (IC). "This not only eliminates the need for electrolytes and precise eluent make-up, but it avoids many of the detection problems that ionic eluents can impose" [1].

Saunders and Pecsok used a tightly crosslinked polyacrylamide gel packed column to achieve ion separation using water as the mobile phase [2]. The results of this successful separation were published 7 years earlier than the paper entitled "Novel ion-exchange chromatographic method using conductometric detection" dealing with a "suppressing" technique [3]. The water mobile-phase IC (WMP-IC) technique developed first is much simpler and has greater potential than the "suppressing" IC technique. However, WMP-IC did not become as widely used or sophisticated as "suppressing" IC.

Two major difficulties have hindered the further development of WMP-IC: (i) ions in low concentrations are difficult to separate. This has been overcome by the addition of a large amount of a particular "sacrifice" ion to the original sample solution [4]; (ii) the analyte ions dis-

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tribute into a "confusing" variety of ion pairs. An earlier solution to the second problem, suggested by Small [1], is the conversion of all cations (or all anions) to a common ion using an ion-exchange column inserted between the sample injection valve and the separating column. Such a pretreatment technique solves the problem of the "confusing" variety of ion pairs, but it diminishes the simplicity of WMP-IC, which is its most significant advantage.

A completely new, simple and convenient approach to overcome the second difficulty derives from an understanding of the partitioning behaviour of analyte ions [5] described in this paper. (Our previous study [5] focussed only on the partitioning behaviour of the analyte ions in WMP-IC; the possibility of partitioning control was not investigated.) A soluble inorganic salt is added to the original sample solution as a source of counterions (introduced ions). This creates a situation in which one of the species of analyte ions to be eluted (target ions) combined with one species of introduced ion has the highest "priority" of formation. When the ratio of the amount of introduced ions to the amount of the species of target ions is sufficiently high (depending on the sample situation), all target ions will be exclusively coupled with the introduced ions. This can be described as "exclusive" partitioning.

This paper outlines the technique by which exclusive partitioning in WMP-IC is achieved.

2. Experimental

2.1. Apparatus

The HPLC system used in this study was a Shimadzu (Kyoto, Japan) LC-6A equipped with a LC-7A pump, a SIL-6A autoinjector, a SCL-6A system controller, a photodiode array UV–Vis detector (SPD-M6A), and a conductivity detector (CDD-6A).

The only column used was the ODS column (L-Column, 250 × 4.6 mm I.D., Chemical Inspection and Testing Institute, Tokyo, Japan) coated with Zwittergent-3-14 (structure shown in Fig. 1). The procedure for the preparation of the zwit-
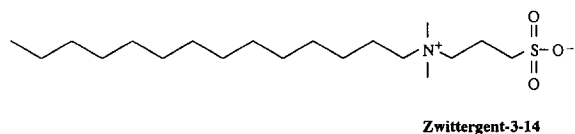

Fig. 1. Structure of zwittergent-3-14.

terionic column was the same as described in the previous paper [6].

2.2. Reagents

Zwittergent-3-14 was purchased from Calbiochem (La Jolla, CA, USA). Inorganic salts, used as the standard analytes, were obtained from Wako (Osaka, Japan). All reagents were used as received. Pure water used to dissolve the reagents and serve as the mobile phase was prepared in the laboratory by a Milli-Q purification system (Millipore, Bedford, MA, USA).

3. Results and discussion

3.1. The interdependent relationship of analytes

In any type of conventional ion chromatography (IC), the time for the elution of an analyte ion species from a certain separation column is determined by the flow-rate and the nature of the mobile phase. In other words, when the column and mobile-phase conditions are fixed, the elution time of any species of analyte ion is fixed. However, in WMP-IC [2,6–8] the sample conditions (species and concentration of the analyte ions) also influence the partitioning and elution of the analyte ions. The following experimental results show the influence of the species of analyte ions on the elution time. When an aqueous solution containing Na^+, Mg^{2+}, Ce^{3+} was separated using WMP-IC with Cl^- as counterion, the cations (Na^+, Mg^{2+}, Ce^{3+}) were eluted in 2.41, 2.72, and 3.12 min, respectively (Fig. 2A). In a sample containing Na^+, Mg^{2+}, Ce^{3+} with NO_3^- as the counterion, the cations (Na^+, Mg^{2+}, Ce^{3+}) were eluted in 3.61, 5.12, and 6.41 min, respectively (Fig. 2B). The influence of
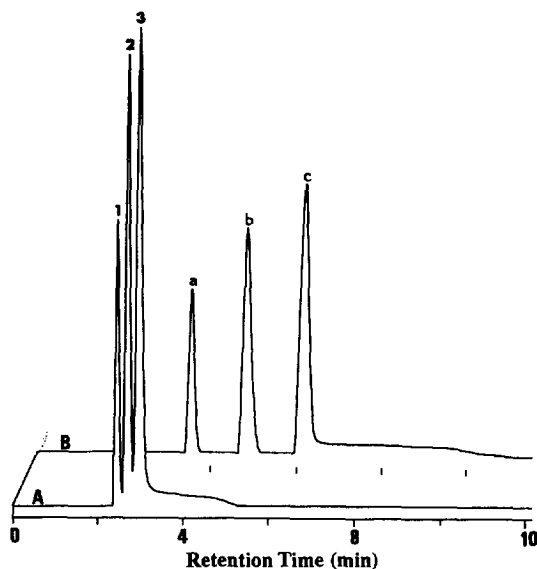
Fig. 2. Chromatograms of (A) an aqueous solution containing 2.0 mM each of Na$^+$, Mg^{2+}, and Ce^{3+} with Cl$^-$ as the counterion and (B) an aqueous solution containing 2.0 mM each of Na$^+$, Mg^{2+}, and Ce^{3+} with NO$_3^-$ as the counterion. ODS-packed column (250 × 4.6 mm I.D.) coated with Zwittergent-3-14; mobile phase, pure water; flow-rate, 1.0 ml/min; detection, conductivity. Peaks: $1 = $ Na$^+$-Cl$^-$, $2 = $ Mg^{2+}-2Cl$^-$, $3 = $ Ce^{3+}-3Cl$^-$; a = Na$^+$-NO$_3^-$, b = Mg^{2+}-2NO$_3^-$, c = Ce^{3+}-3NO$_3^-$.

the analyte ion concentration on the elution time and the proportion of ion pairs are shown in Fig. 3. When a sample containing 500 mM NaCl, 50.0 mM MgCl$_2$, 0.5 mM CeCl$_3$ and 1.0 mM NaNO$_3$ was separated, all of the NO$_3^-$ ions (0.998 mM) were found in a single ion pair (Ce^{3+}-3NO$_3^-$, Fig. 3A). When the concentration of NaNO$_3$ was 10.0 mM, the NO$_3^-$ ions were found in two ion pairs (1.30 mM of NO$_3^-$ in Ce^{3+}-3NO$_3^-$ and 8.70 mM of NO$_3^-$ in Mg^{2+}-2NO$_3^-$; Fig. 3B). When the concentration of NaNO$_3$ was 30.0 mM, the NO$_3^-$ ions were found in three ion pairs (1.43 mM of NO$_3^-$ in Ce^{3+} − 3NO$_3^-$, 24.1 mM in Mg^{2+}-2NO$_3^-$, and 4.47 mM in Na$^+$-NO$_3^-$; Fig. 3C). Similar results were observed for all species of analyte ions studied using WMP-IC. Hence, in WMP-IC, all elution times [and consequentially the performance of the column, e.g. the height equivalent of a theoretical plate (HETP), etc.] and the concentrations of eluted analyte ions (ion pairs) are relative to the sample situation.
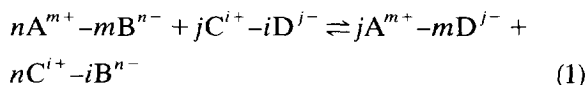
3.2. Adjustment of the sample conditions to create exclusive partitioning

For example, a simple sample contains Na$^+$, Mn^{2+}, Cl$^-$ and NO$_3^-$, and the objective is to determine the Mn^{2+} ions. The Mn^{2+} ions (target ions) may be distributed and eluted as ion pairs of Mn^{2+}-2Cl$^-$ and Mn^{2+} − 2NO$_3^-$. Hence, two calibration graphs, one for Mn^{2+}-2Cl$^-$ and another for Mn^{2+}-2NO$_3^-$, are required. If we increase the concentration of NaNO$_3$ in the sample solution, the Mn^{2+} ions coupled to Cl$^-$ ions (Mn^{2+}-2Cl$^-$) will be released to NO$_3^-$ ions to form Mn^{2+}-2NO$_3^-$ because the "priority" of formation of Mn^{2+}-2NO$_3^-$ is greater than that of Mn^{2+}-2Cl$^-$. As the peak areas in Fig. 4 show, the concentration of Mn^{2+}-2NO$_3^-$ increases to a maximum when the concentration of NaNO$_3$ is greater than 100 mM. In other words, the target ions (Mn^{2+}) have been exclusively coupled (>99.98%) and eluted with NO$_3^-$ ions.

3.3. Other parameters in the partitioning of analyte ions

The effect of coexisting components

The following equation is suggested to express all the possible ion pairs obtained in WMP-IC of an aqueous solution containing A^{m+}, B^{n-}, C^{i+}, and D^{j-} ions:

$$n\text{A}^{m+}\text{-}m\text{B}^{n-} + j\text{C}^{i+}\text{-}i\text{D}^{j-} \rightleftharpoons j\text{A}^{m+}\text{-}m\text{D}^{j-} + n\text{C}^{i+}\text{-}i\text{B}^{n-} \quad (1)$$

When the order of the molal energy for the cations is ΔG A^{m+} < ΔG C^{i+}, and for the anions ΔG B^{n-} < ΔG D^{j-}, the ion pairs expressed on the right side of this equation have greater priority of formation. If the sample solution contains a large proportion of C^{i+} and B^{n-} ions, the formation of the jA^{m+} and mD^{j-} ion pair is inhibited. This was experimentally confirmed. A series of aqueous solutions containing a constant concentration (1.0 mM) of MgCl$_2$ and different concentrations of NaCl/NaNO$_3$ was prepared and separated. The concentration of the ion pair Mg^{2+}-2NO$_3^-$ in each separation was calculated from the calibration graphs derived from the
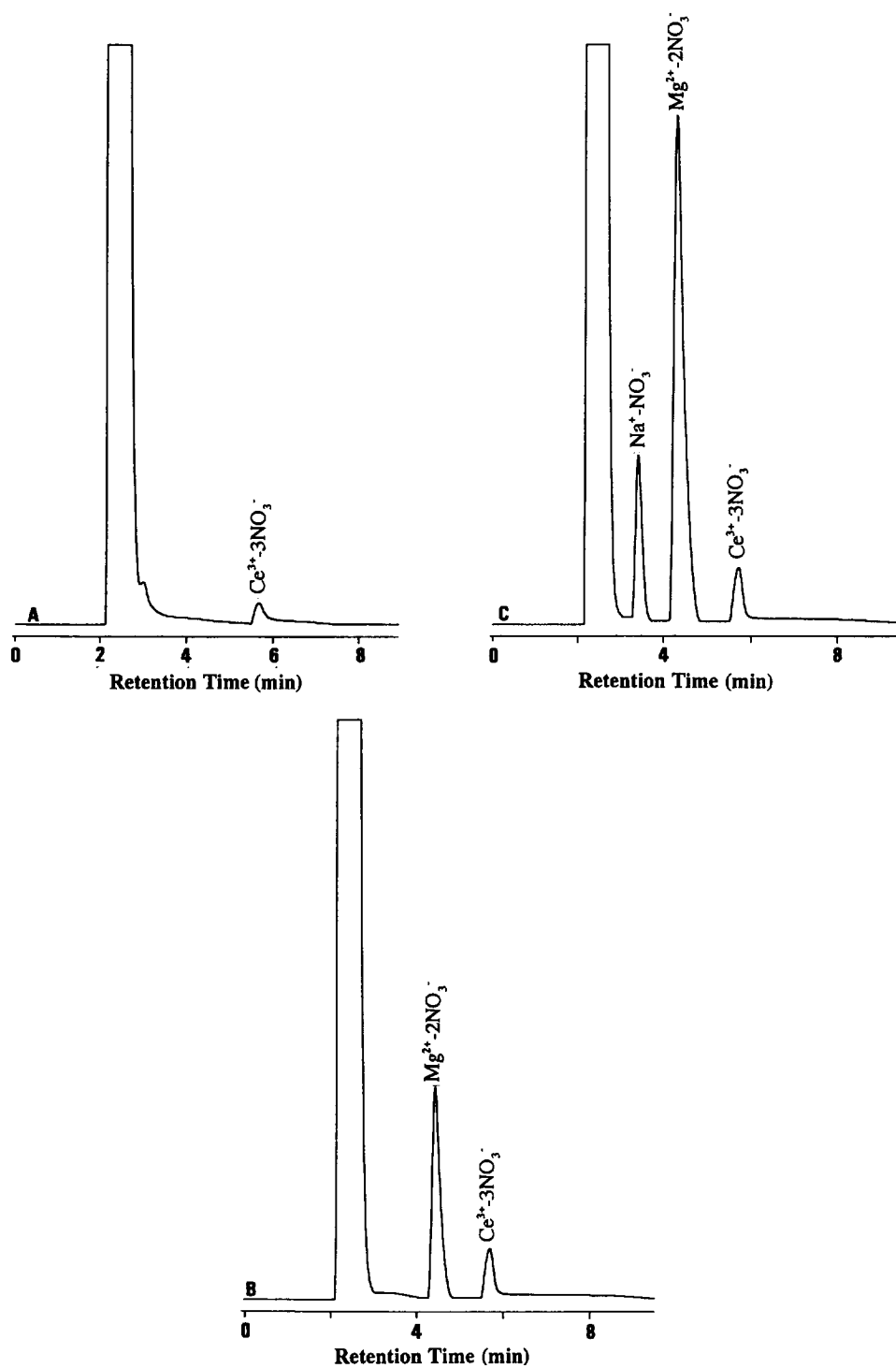
Fig. 3. Chromatograms of aqueous solutions containing 500 mM NaCl, 50.0 mM MgCl$_2$ and 0.5 mM CeCl$_3$ together with NaNO$_3$ (A, 1.0 mM; B, 10 mM; and C, 30 mM). Separation and detection conditions are the same as in Fig. 2.
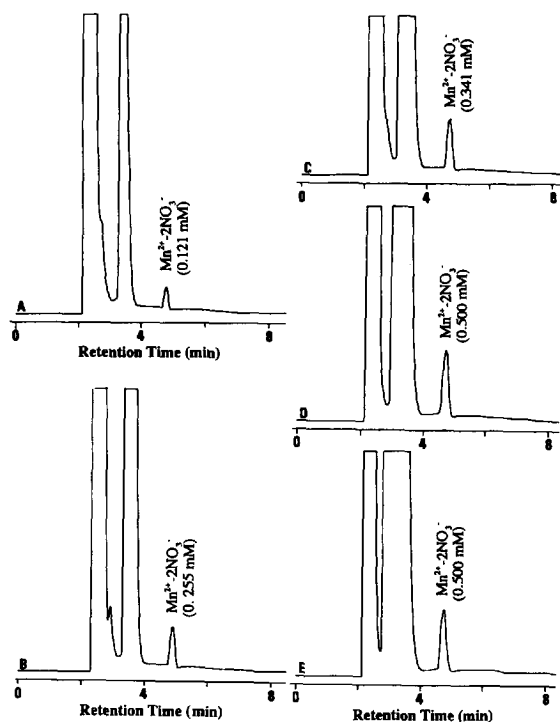
Fig. 4. Chromatograms of aqueous solutions containing 500 mM NaCl, 0.5 mM MnCl$_2$ and NaNO$_3$ (A, 10 mM; B, 30 mM; C, 50 mM; D, 100 mM; and E, 250 mM). Separation and detection conditions are the same as in Fig. 2.

Fig. 5. Effects of the concentration of NaCl (initially involved in MgCl$_2$/NaNO$_3$ mixed solution) on the concentration of newly produced ion pair Mg^{2+}–2NO$_3^-$.

separation of the pure component of Mg(NO$_3$)$_2$ and was plotted as a function of the concentration of NaNO$_3$ in the original sample solution (Fig. 5).

Chemical interactions

When any chemical interaction between the target analyte ions and the other coexisting ion in the sample solution occurs, exclusive partitioning of the target ion cannot be obtained. For example, the experimental results indicated that the target ions (Mn^{2+}) in solution with Na$^+$, SO$_4^{2-}$, Cl$^-$, and NO$_3^-$ were not exclusively coupled with NO$_3^-$ even though the [NO$_3^-$]/[Mn^{2+}] ratio was sufficiently high. This is because some of the Mn^{2+} ions combine with SO$_4^{2-}$ resulting in precipitation.

Newly introduced counterions

Four aqueous solutions were prepared and separated under the same conditions: (i) 0.5 mM
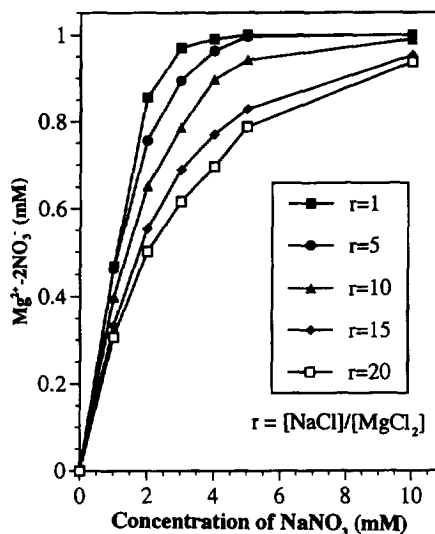
MgCl$_2$ and 5.0 mM NaNO$_2$, (ii) 0.5 mM MgCl$_2$ and 5.0 mM NaBr, (iii) 0.5 mM MgCl$_2$ and 5.0 mM NaNO$_3$, and (iv) 0.5 mM MgCl$_2$ and 5.0 mM NaI. As the chromatograms in Fig. 6 show, the species of counterion coupling with Mg^{2+} ions can be changed with the addition of different introduced ions (NO$_2^-$, Br$^-$, NO$_3^-$, and I$^-$). In principle, any analyte ion species can be exclusively coupled with one species of introduced ion (C^{i+} or D^{j-}). However, for both the introduced cation and anion, its molal energy (ΔG C^{i+} and ΔG D^{j-}) must be the highest among the cations and the anions in the sample solution, respectively.

Charge of the cations

A series of aqueous solutions containing NaNO$_3$, MgCl$_2$, CaCl$_2$, MnCl$_2$, FeCl$_2$, CoCl$_2$, NiCl$_2$, CuCl$_2$, and ZnCl$_2$ was prepared with the objective to determine the divalent cations. Experimental results indicated that when the ratio of [NO$_3^-$]/[M^{2+}]$_T$ ([M^{2+}]$_T$ denoting the total concentration of divalent cations) was larger than 10, these eight species of divalent cations were exclusively coupled and eluted with NO$_3^-$ ions, simultaneously. Different species of cations could not be separated when they had the same charge. However, a group of these divalent cations was
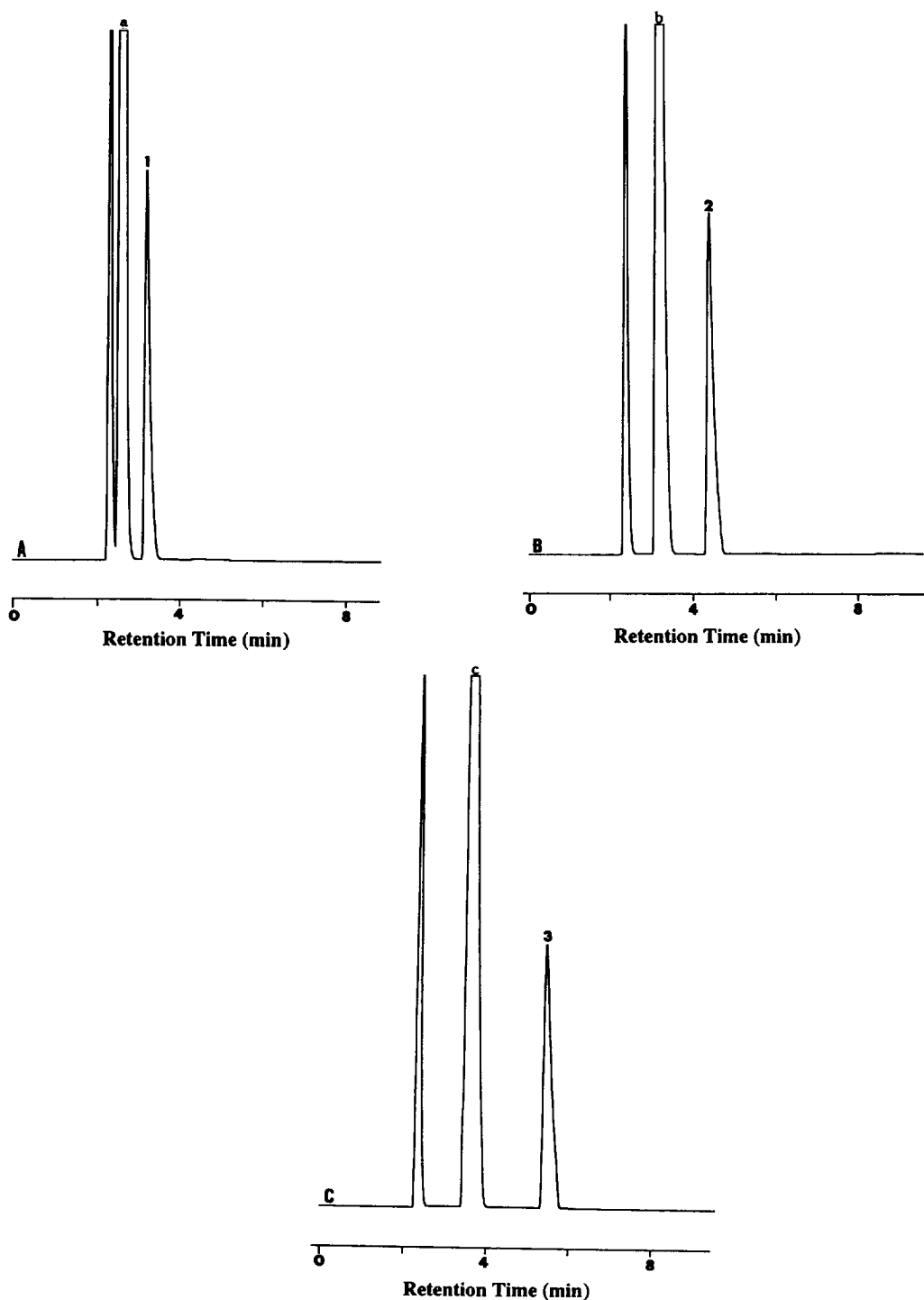
Fig. 6. Chromatograms of an aqueous solution containing (A) 0.5 mM $MgCl_2$ and 5.0 mM $NaNO_2$, (B) 0.5 mM $MgCl_2$ and 5.0 mM NaBr, (C) 0.5 mM $MgCl_2$ and 5.0 mM $NaNO_3$, and (D) 0.5 mM $MgCl_2$ and 5.0 mM NaI. Separation and detection conditions are the same as in Fig. 2. Peaks: a = Na^+–NO_2^-, 1 = Mg^{2+}–$2NO_2^-$; b = Na^+–Br^-, 2 = Mg^{2+}–$2Br^-$; c = Na^+–NO_3^-, 3 = Mg^{2+}–$2NO_3^-$; d = Na^+–I^-, 4 = Mg^{2+}–$2I^-$.
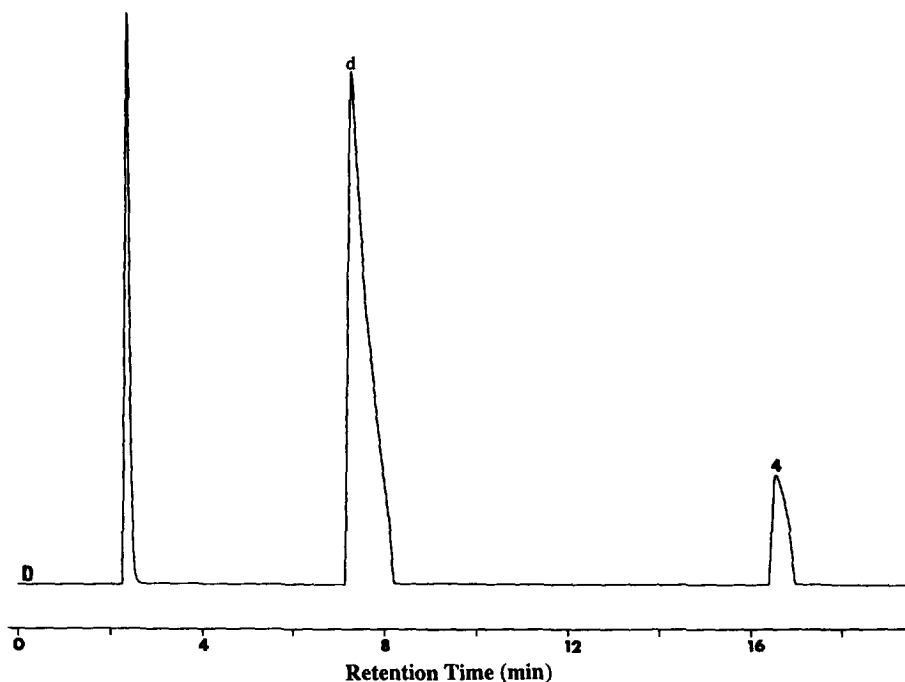
Retention Time (min)

Fig. 6. (Continued)

separated from NaCl. This gives a new approach for on-line elimination of matrix (especially NaCl) in ICP-AES and/or ICP–MS.

4. Conclusion

The partitioning of analyte ions is a controllable procedure. Controlling the species and the concentrations of ions in the sample solution means that exclusive partitioning can be achieved. The species of the counterion coupling with the target analyte ions can be changed at will. This flexibility of formation of ion pairs further demonstrates the efficacy of WMP-IC. This approach can be used to regulate the retention time of analyte ions precisely without changing the chromatographic conditions. This gives a procedure for on-line elimination of concentrated matrix (salts, especially NaCl) in ICP-AES and/or ICP-MS. The technique of recombination of ion pairs also provides a method for synthesizing inorganic salts. It supplies a method for the indirect detection of non-UV-

absorbing ions using UV-absorption detection, by coupling with counterions that are UV-absorbing. Finally, it should be noted here that the problem of unknown "sample conditions" may be met in practical applications of this method. This can, however, be overcome by initial screening of the samples using WMP-IC where the information about the analyte ions can be obtained in advance.

References

[1] H. Small, Ion Chromatography, Plenum Press, New York, 1989, p. 132.
[2] D. Saunders and R.L. Pecsok, Anal. Chem., 40 (1968) 44.

[3] H. Small, T.S. Stevens and W.C. Bauman, Anal. Chem., 47 (1975) 1801.

[4] W. Hu, A. Miyazaki, H. Tao, A. Itoh, T. Umemura and H. Haraguchi, Anal. Chem., 67 (1995) 3713.

[5] W. Hu, T. Tao and H. Haraguchi, Anal. Chem., 66 (1994) 2514.

[6] W. Hu, T. Takeuchi and H. Haraguchi, Anal. Chem., 65 (1993) 2204.

[7] E. Blasius, K.-P. Janzen, W. Adrian, G. Klautke, R. Lorscheider, P.-G. Maurer, V.B. Nguyen, T. Nguyen Tien, G. Scholten and J. Stockemer, Z. Anal. Chem., 284 (1977) 337.

[8] H. Small, M.E. Soderquist and J.W. Pischke, U.S. Patent, 1988, No. 4, 732, 686.