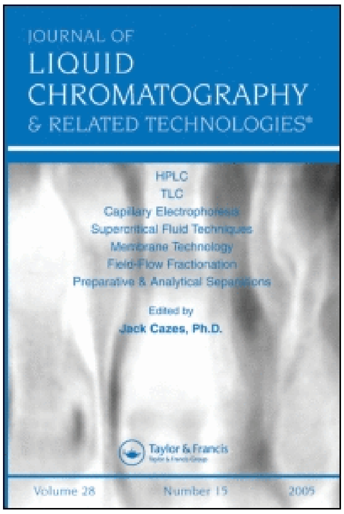

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DETERMINATION OF INORGANIC ANIONS BY ELECTROSTATIC ION CHROMATOGRAPHY WITH A CATION EXCHANGE COLUMN AS A PRE-COLUMN FOR CONVERSION OF THE CATIONS INTO A COMMON SPECIES

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ABSTRACT

The problem of "multiple" distribution of the analyte ions encountered in the separation of inorganic ions by electrostatic ion chromatography (EIC) was overcome. EIC is a new type of ion chromatography (IC) where zwitterionic molecules are used as the stationary phase and pure water serves as the mobile phase. Both ions and polar organic compounds can be separated by EIC and the simultaneous electrostatic attraction-repulsion interactions between the positive-negative charges (or polarities) of the analytes and the stationary phase are considered to be the main mechanisms for the separation.

In the analysis of inorganic ions by EIC, each species of the cation and/or anion was distributed to all species of the counter-ion and co-eluted as pairing ions. To avoid such "multiple" distribution of the analyte ions, the analyte cations were converted into a common species of either Na^+ or Mg^{2+} by using conventional cation exchange columns as the pre-column.

The analyte anions were excellently separated by this method and, furthermore, "exclusive" distribution (single peak per one species of anion) was obtained. Real sample (underground water) was analyzed in duplicate using a conventional anion-exchange IC and this proposed method and identical results were obtained.

INTRODUCTION

Determination of inorganic ions has been carried out by ion-exchange chromatography (IC) with many devices since the middle 1970’s. Detection of inorganic ions with high sensitivity, suppressor or non-suppressor system was invented and hence has given great results and is still being use.

The suppressor system, which is agreeable to conductivity detector, was developed by Small et al.[1-3] and the non-suppressor system, still widely used today, was devised by Gjerde et al.[4] However, they both need elution by other electrolytes which have conductance for the occurrence of ion exchange. Consequently this seems to promote the back ground noise to a high level.

An analysis of inorganic cations at low concentration by HPLC was performed recently with an induced coupled plasma emission spectrometry (ICP-AES) or mass spectrometry (ICP-MS) as a detector. It allowed the determination of inorganic cations with no special pre-treatment even when the concentration of sample solution is very low.[5,6]

Sensitive determination of inorganic cations is achieved by ICP-AES or ICP-MS coupled with HPLC; that of anions has not yet been carried out. In a sense of this problem, EIC has a possibility of sensitive analysis for inorganic anions since it maintains low background noise. The superiorities of EIC have been introduced in previous papers[7-9] so it is likely to become more popular.

However in EIC, the ion redistribution occurs among all analytes during the separation since the mobile phase consists of no electrolytes.[10] As a result, more than one peak corresponds to the same species of the analyte anions observed and disturbs the qualification and quantification of inorganic anions.

To eliminate this problem, we used conventional cation exchange columns as a pre-column, in order to convert the analyte cation into a common species, and to obtain a single peak per anion. The method reported in this paper is one of the technique which makes EIC a practically useful conventional IC method.

EXPERIMENTAL

Apparatus

The liquid chromatographic system used in this study was a conventional LC system, obtained from Shimadzu (Kyoto, Japan). It consisted of a pump (LC-10A), a sample injector (Rheodyne 7161,California) with a 100-µL loop, a conductivity detector (CDD-6A), an UV-Vis detector (SPD-10A). A Chromatopack CR-6A was also employed for data treatment. An ODS packed column, L-column, 4.6×250mm, (Chemical Inspection and Testing Institute, Tokyo, Japan) coated with Zwittergent 3-14 micelles was prepared and used as a separation column. The procedure for the preparation of the column was described in a previous paper.[7] Two conventional cation exchange columns, one was a Shim-pack6A (4.6×100mm) with function groups of carboxyl and the other was a SP-420N (4.6×35mm) with sulphonic groups, were used for converting the analyte cation into a common ion. These were obtained from Shimadzu (Kyoto, Japan) and Showa Denko (Tokyo, Japan), respectively. A guard column, 4.6×10mm, (Chemical Inspection and Testing Institute, Tokyo, Japan) was also used for protecting the cation exchange columns and the separation columns in this IC system.

The flow rate of the mobile phase was 1.0 mL/min. The injection volume of samples was always the same as the injection loop volume. All of the separations were carried out at room temperature. The atomic adsorption spectrometer (AAS) used for evaluating the counter-ion (cation) of the targeted analytes (anions) was Hitachi 170-50 (Tokyo, Japan).

Reagent

The zwitterionic detergent of Zwittergent3-14 was obtained from Calbiochemical (La Jolla, CA, USA). Inorganic salts used as the standard analytes were obtained from Wako (Osaka, Japan). All reagents were analytical reagent-grade and were used without further purification. Pure water used in this study to dissolve the reagents and serve as the mobile phase was prepared in the laboratory by a Mill-Q purification system (Millipore, Bedford, MA, USA). All of the samples and the pure water used as the mobile phase were stored in clear polypropylene bottles.

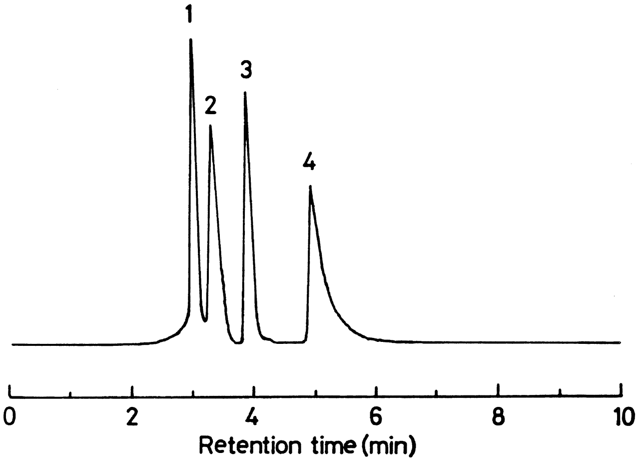

Figure 1. Chromatogram of an aqueous solution contains 1.0mM $NaNO_3$, 0.5mM $CaCl_2$. ODS-packed column (4.6×250mm) coated with Zwittergent3-14; mobile phase, pure water; flow-rate, 1.0ml/min; detection, conductivity. Peaks: 1=Na^+-Cl^-, 3=Na^+-NO_3^-, 2=Ca^{2+}-2Cl^-, 4=Ca^{2+}-2NO_3^-.

Preparation of the Pre-Column

The counter-ion of the cation exchange column was initially converted into Na^+ or Mg^{2+} by injection of ca. 3.0 mL of 10 mM NaCl or $MgCl_2$ aqueous solution into the column. The cation exchange columns were then rinsed thoroughly with pure water as the mobile phase before being connected to the separation column.

RESULTS AND DISCUSSION

Ion Redistribution

As mentioned above, the inorganic cations and anions were coeluted as pairing ions to maintain the electro-neutrality. All possible combinations of the cations and the anions will be obtained and the distribution ratio of cations and anions to each ion combination (pairing ions) was dependent on the ratio of the concentrations of the analyte ions in the original sample solution.

A typical chromatogram of an aqueous solution contains 1.0mM $NaNO_3$ and 0.5mM $CaCl_2$ obtained using EIC is shown in Figure 1. Four ion combinations, i.e., Na^+-Cl^-, Na^+-NO_3^-, Ca^{2+}-2Cl,$^-$ and Ca^{2+}-2NO_3^- were created

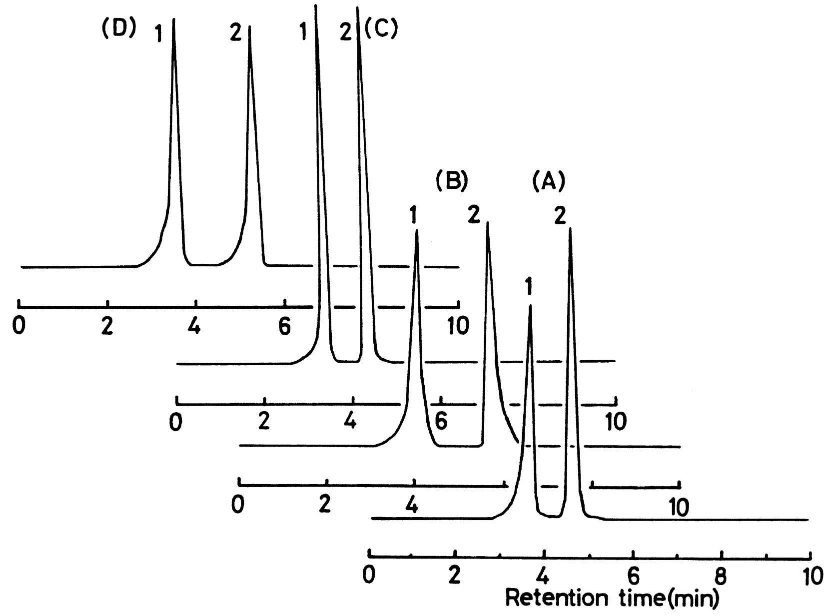

Figure 2. Chromatograms of an aqueous solution containing 1.0mM $NaNO_3$, 0.5mM $CaCl_2$ determined with conversion of the cations into Na^+ or Mg^{2+}. (A) and (B) were obtained using carboxylic type of the pre-column; (C) and (D) were obtained using sulphonic type of the pre-column. Other conditions were the same as described in Figure 1. Peaks: 1= Cl^-, 2= NO_3^-.

and detected. For the same species of the anions (Cl^- and NO_3^-), the ion combination with monovalent cations as the counter-ions was eluted earlier than those combined with divalent cations as their counter-ion. The occurrence of such "multiple" distribution of the analyte ions is certainly a drawback in the quantitative analysis, since calibration curves must be provided for all possible ion combinations. To overcome this practical problem, a small cation exchange column was inserted between the injector and the separation column, in order to convert the analyte cation into a common ion. Monovalent cation of Na^+ and divalent cation of Mg^{2+} were chosen as the typical common counter-ion and separation behaviors were investigated.

Separation of Plural Number Inorganic Ions Mixtures

The same sample solution (described in Figure 1) was then analyzed using the same EIC with the device of cation converting. Figure 2A, 2C shows the separation result obtained using Na^+ as the common counter-ion; while Figure

Table 1

The Reproducibility of the Two Types of the Pre-Column

	Standard Solution		Underground Water	
	Concn. (mM)	RSD(%)	Concn. (mM)	RSD(%)
1. Pre-Column (COO^-), Counter Cation; Na^+				
SO_4^{2-}	---	---	0.94	3.17
Cl^-	1.08	2.64	0.85	3.07
NO_3^-	0.99	2.71	0.48	3.69
2. Pre-Column (SO_3^-), Counter Cation; Na^+				
SO_4^{2-}	---	---	0.96	3.43
Cl^-	1.05	2.06	0.86	2.86
NO_3^-	1.08	2.22	0.53	2.46

2B, 2D shows the result obtained using Mg^{2+} as the common counter-ion. An exclusive elution of the analyte anions (a single peak per anion) was obtained. When the sample was injected into the pre-column, the analyte anions were eluted immediately together with Na^+ or Mg^{2+} as their counter-ion, due to Donnan exclusion by the carboxylic or sulphonic groups fixed on the stationary phase.

The fraction of each ion combinations were collected and analyzed by AAS; response due to the original counter-ion (Ca^{2+}) was not observed. From this fact, we were convinced that the analyte cations were completely converted into the Na^+ or Mg^{2+} by the pre-column.

Satisfactory results of separation were obtained with using either Na^+ or Mg^{2+} as the common counter-ions, but the separation efficiencies were found to be different. The divalent cation (Mg^{2+}) always gave a higher separation efficiency than the monovalent cation (Na^+). Whereas the high separation efficiency was observed with Mg^{2+} as the common counter-ion, we decided to use Na^+ as the common counter-ion for further retention behavior investigation and for the practical application. The sufficiently high separation efficiency was also obtained and, further more, that the elution of the ion combination was faster when Na^+ was used as the common counter-ion.

Both carboxylic and sulphonic type of the pre-columns showed excellent results for the analysis of plural inorganic ion mixtures. However, as opposed to our supposition, peaks with better symmetry and sharpness were observed by

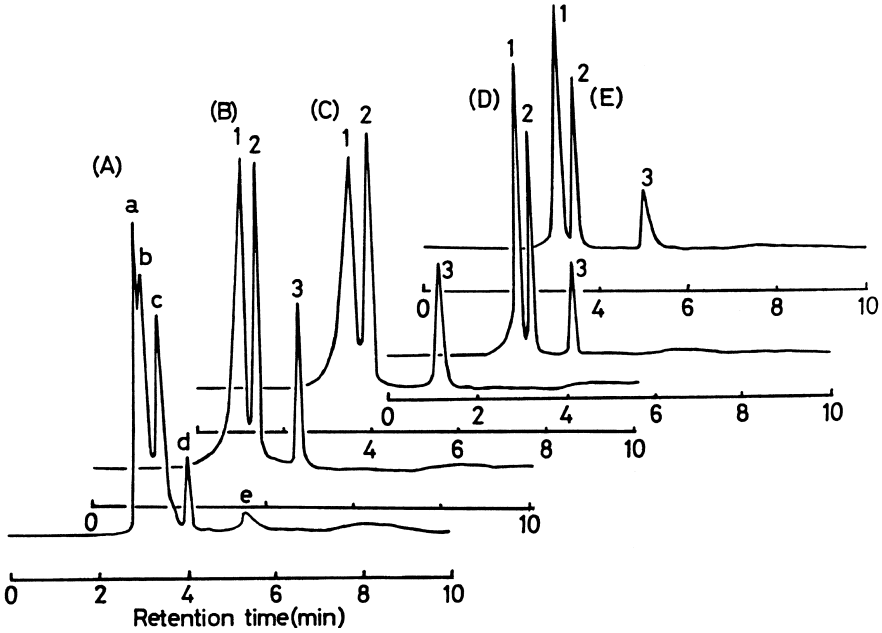

Figure 3. Chromatogram of underground water determined by EIC. (A) was obtained with analytical column alone, (B) and (D) were with conversion of cations into Na^+ obtained using carboxylic type of the pre-column; (C) and (E) were with conversion of cations into Mg^{2+} obtained using sulphonic type of the pre-column. Other conditions were the same as described in Figure 1. Peaks: a=$2Na^+$-SO_4^{2-}, b=Na^+-Cl^-, c=Ca^{2+}-$2Cl^-$, d=Na^+-NO_3^-, e=Ca^{2+}-$2NO_3^-$1=SO_4^{2-}, 2= Cl^-, 3= NO_3^-.

using the sulphonic type of the pre-column. This can be explained from the fact that the length of the two columns is different. The longer the column becomes, the diffusion effect of the ions in the pre-column increases. Except for this, the two types of ion exchange groups showed no remarkable variations in the analysis of the plural number of inorganic ion mixtures.

The carboxylic type of the pre-column pretreated with Na^+ or Mg^{2+} as the common counter-ion endured at least 40 analyses inorganic ion mixtures with one pre-treatment, whereas the sulphonic type did only about 20 analyses.

This phenomenon may have a close relation to the ion exchange capacity of the conventional cation exchange columns. However it was not investigated any further in this study. As shown in Table 1, the value of the Relative Standard Deviation (RSD) falls in the range 0~4%.

Table 2

Comparison of the Concentration (mM) of the Anions in Underground Water Determined by EIC Coupled with Pre-Column and Conventional IC, Respectively

	Present Method		Conventional IC
	Pre-Column (COO^-, Na^+ Type)	Pre-Column (SO_3^-, Na^+ Type)	
SO_4^{2-}	0.94	0.96	0.93
Cl^-	0.85	0.86	0.83
NO_3^-	0.48	0.53	0.51

Practical Application

In order to demonstrate the advantages of this technique, underground water was chosen for practical samples determined by EIC. A typical chromatogram is shown in Figure 3. The peaks observed without using a pre-column were too complicated for qualification and/or quantification of the analytes.

However, this difficulty was completely solved when the pre-columns were employed. SO_4^{2-}, Cl^-, and NO_3^- were found in the sample and their concentrations were calculated to be 0.96mM, 0.86mM, 0.53mM from the calibration curves. This sample was also analyzed using Mg^{2+} as the common counter-ion and the identical results were obtained.

To confirm the results obtained by the present method, same sample of the underground water was also examined using conventional anion exchange chromatography and good agreements were obtained (Table 2).

CONCLUSION

Conversion of analyte cation into a common species using a small cation exchange column as the pre-column is a simple but effective method for carrying on EIC into a new stage of practical application. The method connecting conventional cation exchange column with a zwitterionic column can also be expected as a unique method for simultaneous separation of inorganic cations and anions with a single run using aqueous solution as the mobile phase.

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