

On-Line Removal of Interfering Alkaline Earth Metals for Simultaneous Determination of Hydrogen Carbonate, Chloride, Nitrate and Sulfate by Indirect Photometric Detection Ion Chromatography

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Indirect photometric detection ion chromatography has been used in the determination of ionic compounds in combination with a conventional high-performance liquid chromatographic (HPLC) system.¹ One advantage of this method is that the sensitivities of conjugate bases of weak acids are as high as those of strong acids.² Therefore, this method is especially useful for the simultaneous determination of strong and weak acids.³ By bubbling nitrogen gas through the eluent to remove atmospheric carbon dioxide from the system, hydrogen carbonate and other anions such as chloride, nitrate and sulfate in environmental samples can be determined simultaneously with sensitivity.⁴ However, in environmental water analyses by the previous system, samples which contained large amounts of magnesium(II) and calcium(II) gave interfering peaks, since these metal ions form complexes with eluent compounds such as phthalate and trimesate.⁵ A possible clean-up treatment available for them is to use a cation exchange cartridge. This off-line treatment, however, is tedious and requires a large sample volume.

To remove these disadvantages, we inserted a cation exchange column just before the analytical column in the previous system.⁴ Although interfering peaks were removed, peak resolutions of analyte anions were reduced due to the cation exchange column. Column-switching technique⁶ resolved this problem effectively. By adding another switching valve and a loop between the two columns, interfering peaks were completely removed without any decrease in peak resolution. The purpose of this report is to describe the efficiency of this proposed system.

Experimental

Chemicals

All chemicals used were of analytical reagent grade. Water was purified with a Millipore (Bedford, MA, USA) Milli-Q system.

HPLC system and its conditions

Configuration of the HPLC system used is shown in Fig. 1. The system consisted of a nitrogen gas bomb (B), a gas washing bottle (W), an eluent (and carrier) reservoir (R), JASCO (Tokyo, Japan) 880-PU pumps (P₁, P₂), a Rheodyne (Cotati, CA, USA) 7125 injector (V₁) with a 300- μ l loop (L₁), a removal column (C₁, 30 \times 4.6 mm i.d.), a JASCO 892-01 switching valve unit (V₂) with a 20- μ l loop (L₂), an analytical column (C₂, 50 \times 6.0 mm i.d.), a JASCO 860-CO column oven (O), a JASCO 870-UV variable wavelength absorbance detector (D) and a Shimadzu (Kyoto, Japan) C-R3A integrator (I). The switching time of V₂ was automatically controlled by a JASCO 801-SC system controller.

C₁ was packed with Mitsubishi Kasei (Tokyo, Japan) MCI GEL CK-10S (styrene-divinylbenzene copolymer with a cation exchange capacity over 1.9 meq/g). C₂

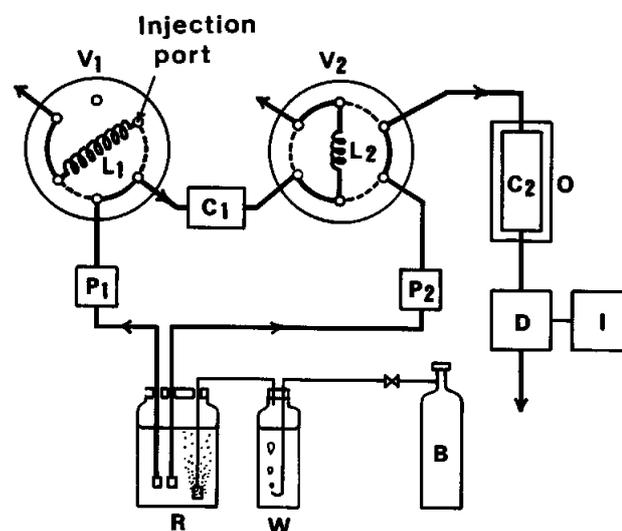


Fig. 1 Schematic diagram of the proposed system. Abbreviations are described in the text.

was packed with MCI GEL SCA-03 (polyacrylate polymer with an anion exchange capacity of 30 $\mu\text{eq/g}$) which was kept at 40°C. The eluent was 1.0 mM phthalic acid -0.15 mM *N*-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid (HEPES) buffer (pH 7.0 \pm 0.1). The same solution was used also as a carrier to send the sample solution into C_1 . Flow rates of P_1 and P_2 were set at 0.5 and 1.0 ml/min, respectively. The detection wavelength was 260 nm. Other conditions were the same as in our previous report.⁴

Operating procedures

Both C_1 and C_2 were conditioned with the eluent when both V_1 and V_2 were at their initial positions (solid line in Fig. 1). The sample solution was injected into L_1 , and then sent to C_1 by switching V_1 (dotted line). Alkaline earth metal ions were bound to the column, while anions were eluted. When the subject anions flow through L_2 (1 min after the sample injection), an aliquot of the fraction was taken and transferred into C_2 by switching V_2 (dotted line). The anions were separated and then detected with an indirect photometric process. Twenty minutes after the sample injection, both valves were returned to their initial positions.

Results and Discussion

Recently heart-cutting recycling has been used in ion chromatography to determine trace nitrite in brine.⁷ In the report, a nitrite fraction from the analytical column, still containing a high concentration of chloride, was collected in a loop, and then injected again into the analytical column. The cutting loop required a large volume to collect the fraction after the first separation completely. This resulted in the peak's broadening and its height decreasing after the second separation. In contrast to that work, the diffusion of subject anions in our work is much smaller, even after passing through C_1 , since anions have no affinity to the remover column. Moreover, the cation exchange capacity of the column used is large enough for multiple injections as described below. These facts enable the volume of the cutting loop to be smaller than that of the sample loop. In our system, L_2 collects an aliquot of the treated sample from C_1 and then transfers it into C_2 .

Figure 2 shows recorder response of 0.5 mM sodium chloride vs. switching time of V_2 with a volume of 20 μl for L_2 . Ideal rectangle profiles were not observed for three different given volumes (100, 300 and 500 μl) of L_1 . Although this result indicated the diffusion in both L_1 and C_1 , response curves showed plateaus from 50 s to 70 s for 300 μl and from 50 s to 90 s for 500 μl . Thus, the determination reproducibility and accuracy might be better if the switching time occurred during the plateau stage rather than the steep stage. On the other hand, the binding of alkaline earth metal ions to C_1 suggests that the life time of the column is prolonged by decreasing the volume of L_1 . Taking these things into consideration,

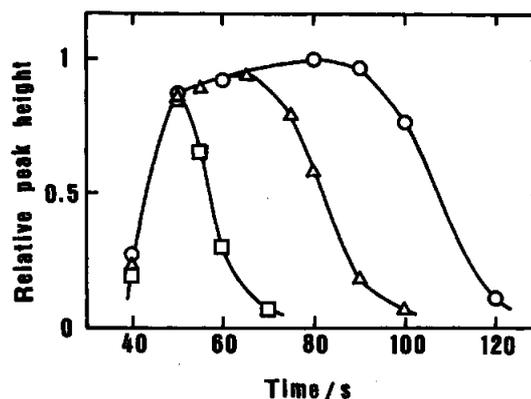


Fig. 2 Detector response of sodium chloride vs. switching time of V_2 . Volume of L_1 : \square , 100 μl ; Δ , 300 μl ; \circ , 500 μl . Volume of L_2 , 20 μl . Sample concentration, 0.5 mM.

we used a volume of 300 μl for L_1 and a switching time of 60 s.

The effect of the present system to reduce peak-broadening is clarified by comparing width at half-peak height ($W_{h/2}$) of anions by systems with/without V_2 . The difference was larger for anions which had stronger retention. $W_{h/2}$ values of both hydrogen carbonate and chloride were respectively 15% and 6% smaller by the system with V_2 than those without V_2 . The difference was less than 1% for sulfate.

Under the above conditions, relative standard deviation were less than 2% ($n=5$) for the three anions (each anion concentration was 0.1 mM). Detection limits (signal-to-noise ratio was three) were 20 μM for nitrate and 10 μM for hydrogen carbonate, chloride and sulfate. The limits became smaller without any significant decrease in peak resolution with increasing the volume of L_2 up to 100 μl .

Chromatograms of Sai-river (Kanazawa) water, containing both magnesium (0.05 mM) and calcium (0.17 mM), with the present/previous systems are compared in Fig. 3. When the previous system was used, the interferences were observed as negative (5 min and 7 min) and positive (15 min) peaks (Fig. 3B). Magnesium ion gave both peaks at 5 min and 15 min, and calcium ion gave both peaks at 7 min and 15 min. These interfering peaks were removed completely when the proposed system was used without any subsequent decrease in peak resolution (Fig. 3A).

The calculated capacity of C_1 (1.9 meq) would enable over 3000 injections of 300 μl of 1 mM alkaline earth metal ion. In our laboratory, the column was used continuously for routine environmental water analyses. Peak widths of the four anions did not increase and neither magnesium nor calcium ions were eluted from the column over a month. This result suggests that the capacity of C_1 is quite sufficient for practical use. The exhausted column, if necessary, can be easily regenerated with 100 ml of 0.1 M ethylenediaminetetraacetic acid disodium salt.

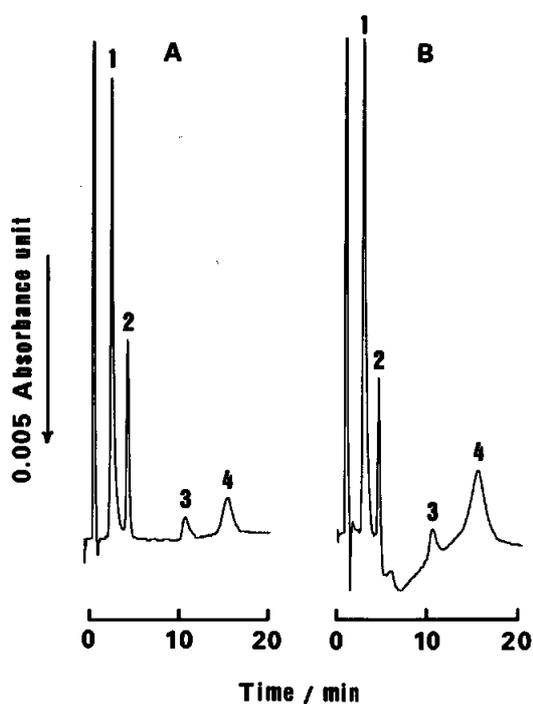


Fig. 3 Chromatograms of river water by (A) the proposed and (B) the previous systems. Peaks: 1, hydrogen carbonate (0.6 mM); 2, chloride (0.15 mM); 3, nitrate (0.06 mM); 4, sulfate (0.05 mM).

Similar interfering peaks of alkaline earth metal ions were observed in anion chromatography with conductivity detection using such eluent compounds as phthalate and gluconate. The same metal-complex formation was considered to be the reason, and the interfering peaks were also removed by the proposed system.

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