

## Simultaneous Determination of Anions and Cations in Natural Water by Ion-exclusion/Cation-exchange Chromatography with a Weakly Acidic Cation-exchange Resin Column

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The simultaneous determination of anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) in natural water obtained by Nakdong River waters system in Korea were performed by ion-exclusion/cation-exchange chromatography with conductimetric detection. The stationary phase was a polymethacrylate-based weakly acidic cation-exchange resin column in the  $\text{H}^+$ -form and a weak-acid eluent. When using only a 1.4 mM sulfosalicylic acid/6 mM 18-crown-6 ether as an eluent, good resolution of both anions and cations, minimum time required for the separation, and satisfactory detection sensitivity were obtained in a reasonable time. The method was successfully applied to the simultaneous determination of anions and cations in natural waters.

**Key Words :** Ion-exclusion/cation-exchange chromatography, Weakly acidic cation-exchange resin, Simultaneous determination of anions and cations

### Introduction

Ion chromatography has been recognized as a useful approach for the determination of anions and/or cations in many types of natural waters such as acid rains.<sup>1</sup> Tanaka and coworkers<sup>2-8</sup> reported that the simultaneous ion-exchange chromatography (IEC)/cation-exchange chromatography (CEC) can be performed on a weakly acidic cation-exchange resin column using a single sample injection, resulting in the simultaneous determination of anions and cations commonly found in acid rain water. They suggested that the concentration and kind of the eluent is a very important factor for both the ion-exclusion chromatographic separation of anions and the cation-exchange chromatographic separation of cations. An eluent with a weak acid such as tartaric acid was used for separation of anions and cation in acid rains by IEC/CEC. Furthermore, an eluent with a strong acid such as sulfosalicylic acid was used for separation of anions and cations in acid rains by IEC/CEC.

On the other hand, we firstly reported on the simultaneous determination of anions and cations in acid rain waters by high-performance IEC/CEC with conductimetric detection using a single sample injection.<sup>5,9</sup> Good resolution was obtained when the eluent was a mixture of strong acid and chelating agents. However, little research has been studied on an optimal condition of eluents and the simultaneous determination of anions and cations in natural water caused by acid rain by IEC/CEC.

In this study, the simultaneous determination of anions and

cations in natural water as model samples obtained by Nakdong River water system was performed by high-performance IEC/CEC with conductimetric detection in a weakly acidic cation-exchange resin column. In order to obtain good resolution, the resolutions condition such as acidic eluent concentration and eluent composition were investigated.

### Experimental Procedures

**Instrumentation.** The ion chromatography system used in this work consists of Waters TM 600 Pump operating at 1-1.2 mL/min, Rheodyne Model 7725i injection valve equipped with a 100  $\mu\text{L}$  sample loop, Waters 600 Controller, Column oven operated at 25 °C with Waters Temperature Control Module, Waters 431 Conductivity Detector. System control as well as data collection and processing are done by Young Lin Autocro-Win Data Module.

**Columns.** For simultaneous IEC/CEC separation of both anions and cations, the column was carried out using 300 mm  $\times$  7.8 mm (I.D) TSKgel OA-PAK-A (Tosoh, Tokyo, Japan) weakly acidic cation-exchange columns. These columns were packed with polymethacrylate-based weakly acidic cation-exchange resin in the  $\text{H}^+$ -form (5  $\mu\text{m}$  particle size, 0.1 meq./mL).

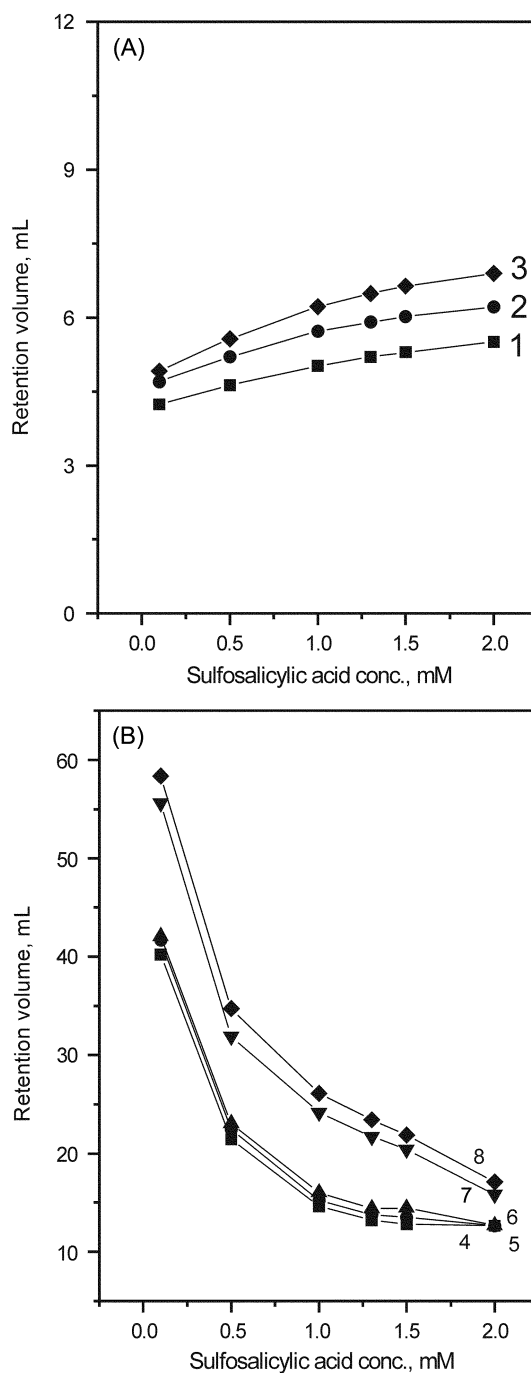
**Reagents and Sampling.** For simultaneous separation of anions and cations, the eluent was prepared by diluting 100 mM sulfosalicylic acid and 100 mM crown ether prepared by dissolving sulfosalicylic acid and 18-crown-ether (1,4,7,10,13,16-hexaoxacyclooctadecane) in deionized water. For the preparation of standard solutions of the desired anions and cations, commercially available analytical-reagent grade

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chemicals were used. Samples of river water were collected in Nakdong River, one of the major rivers of Korea, during the period of January through July, 1999 and passed through a 0.45  $\mu\text{m}$  membrane filter before chromatographic analysis.

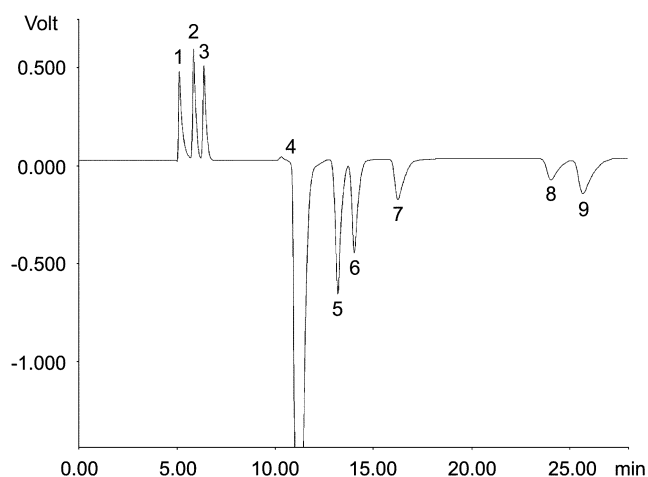
## Results and Discussion

**Effect of Sulfosalicylic Acid Concentration.** In CEC, acidic eluents may be used for the simultaneous separation of mono- and divalent cations on weakly acidic cation-exchange resins.<sup>10-12</sup> These same eluents are also used frequently in IEC for the simultaneous separation of strongly and weakly acidic anions on weakly acidic cation-exchangers.<sup>9-12</sup> Additionally, a conductimetric detector can be used as a universal detector for the detection of both anions and cations. Anions are detected directly and appear as increases in conductance compared to the background, whereas cations are detected indirectly and appear as decreases in conductance compared to the background. Accordingly, it should be possible to determine simultaneously both anions and cations by a combination of IEC and CEC with conductimetric detection on a weakly acidic cation-exchange column. In a previous study,<sup>8</sup> a tartaric acid-methanol-water eluent was found to be the most suitable for the simultaneous separation and detection of the anions and cations. In this study, a strong acid having a hydrophobic nature, such as sulfosalicylic acid was used as eluent for obtain good resolution. The effect of the concentration of sulfosalicylic acid in the eluent on the retention volumes ( $V_R$ ) of the anions and cations was investigated to optimize the simultaneous separation conditions. Retention volume ( $V_R$ ) values of the anions showed a slight increase with increasing concentration of sulfosalicylic acid in the eluent (Figure 1), as expected from the ion-exclusion effect and the resolution of the anions increased. On the other hand, the  $V_R$  values of the cations were decreased significantly on increasing the concentration of sulfosalicylic acid, as expected from the ion-exchange effect. A negative eluent dip was observed for sulfosalicylic acid, with this dip appearing between the peaks of the anions and the peaks of the cations. While such an eluent dip for a strong acid like sulfosalicylic acid is expected to occur at the column void volume,  $V_R$  of the sulfosalicylic acid was larger than a column void volume because of hydrophobic interactions of the eluent species with the unfunctionalised portions of the stationary phase. The background conductance of the eluent was increased with increasing concentration of sulfosalicylic acid in the eluent (278  $\mu\text{S}/\text{cm}$  for a 0.5 mM eluent, 425  $\mu\text{S}/\text{cm}$  for a 1.0mM eluent, and 630  $\mu\text{S}/\text{cm}$  for a 1.4 mM eluent). Since an increase in the eluent conductance also caused a decrease in the sensitivity range of conductivity detection, it was concluded that the lowest possible eluent concentration of sulfosalicylic acid should be used, commensurate with reasonable peak resolution and separation time. After consideration of these factors, it was concluded the optimal concentration range of sulfosalicylic acid for the simultaneous IEC/CEC separation of anions and cations is in the range



**Figure 1.** Effect of sulfosalicylic acid concentration on retention volumes ( $V_R$ ) of common inorganic (A) anions and (B) cations. Columns: TSKgel OA-PAK-A (300 7.8 mm I.D.). Column temperature: 25 °C. Detection: conductivity. Flow rate: 1.2 mL/min. Injection volume: 50  $\mu\text{L}$ . Eluent conductivity: 630 S/cm. Standard sample: mixture of 0.1 mM  $\text{KNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{CaCl}_2$  and 0.05 mM  $\text{Na}_2\text{SO}_4$  and  $\text{MgSO}_4$ . Lines: 1 =  $\text{SO}_4^{2-}$ ; 2 =  $\text{Cl}^-$ ; 3 =  $\text{NO}_3^-$ ; 4 = eluent dip; 5 =  $\text{Na}^+$ ; 6 =  $\text{NH}_4^+$ ; 7 =  $\text{K}^+$ ; 8 =  $\text{Mg}^{2+}$ ; 9 =  $\text{Ca}^{2+}$ .

of 1.0-1.5 mM. Figure 2 shows the simultaneous IEC/CEC separation of anions and cations obtained using a 1.4 mM sulfosalicylic acid / 6 mM crown ether eluent. In this investigation, when using only a sulfosalicylic acid / crown ether as an eluent without methanol, good resolution of both anions and cations was obtained on minimum time required



**Figure 2.** Simultaneous IEC/CEC separation of anions and cations by elution with 1.4 mM sulfosalicylic acid/ 6 mM 18-crown-6-in water at 1.2 mL/min. Peaks: 1 =  $\text{SO}_4^{2-}$ ; 2 =  $\text{Cl}^-$ ; 3 =  $\text{NO}_3^-$ ; 4 = eluent dip; 5 =  $\text{Na}^+$ ; 6 =  $\text{NH}_4^+$ ; 7 =  $\text{K}^+$ ; 8 =  $\text{Mg}^{2+}$ ; 9 =  $\text{Ca}^{2+}$ . Other chromatographic conditions as shown in Figure 1.

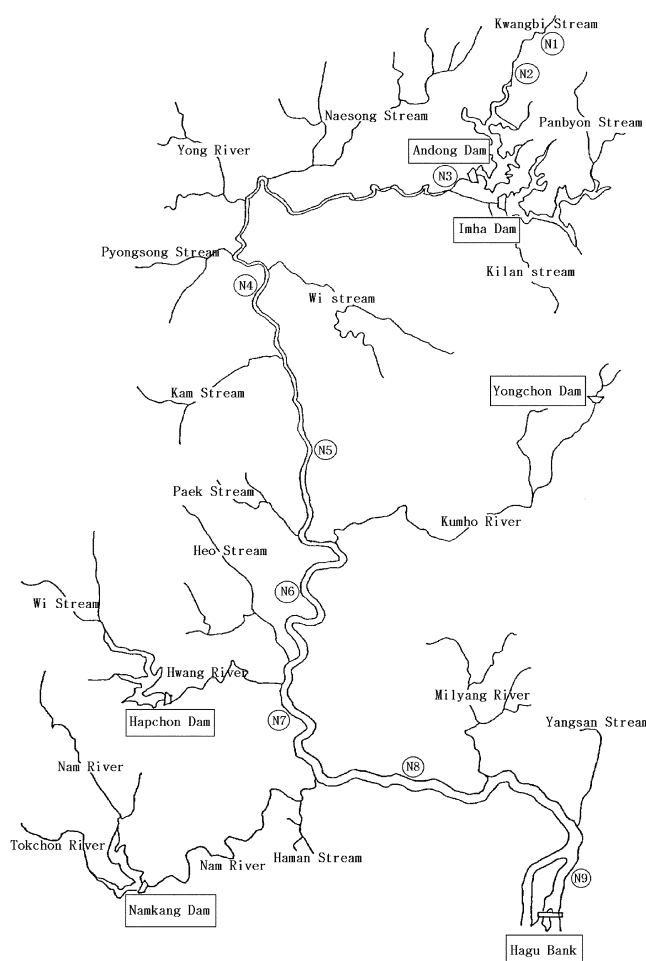
for the separation, and satisfactory detection sensitivity.

**Analytical Performance Characteristics.** The IEC/CEC system at the optimal elution conditions exhibited linear calibration plots of peak area versus concentration for anions and cations over the concentration ranges 0-1.0 mM for anions ( $r^2 = 0.9987$ ) and 0-0.5 mM for cations ( $r^2 = 0.9925$ ). Detection limits calculated at  $S/N=3$  ranged from 7.8-23.8  $\mu\text{g/L}$  for the anions and 7.5-26.3  $\mu\text{g/L}$  for the cations. The reproducibility of retention times at the optimal elution conditions was 0.98-0.13% relative standard deviation (RSD) for anions and 0.15-0.28% for cations, as determined from ten complete chromatographic runs on the same sample. Reproducibility of chromatographic peak areas was 0.84-1.42% RSD for anions and 1.54-1.76% for cations, again for ten chromatographic runs. The poorer reproducibility for cations arises from errors involved in performing area integration on negative peaks.

**Simultaneous Determination of Anions and Cations in Natural Water Obtained from Nakdong River.** The simultaneous determination of anions and cations in natural water obtained by Nakdong River system in Korea was performed by IEC/CEC with a weakly acidic resin column. Table 1 shows four large rivers in Korea, 63,016  $\text{km}^2$  of their total valley area which correspond to about 70% of total national land. The Nakdong river is the longest river with 7,469 km total flow length. The Han River has the greatest valley area of 26,018  $\text{km}^2$ . Figure 3 shows a river valley and

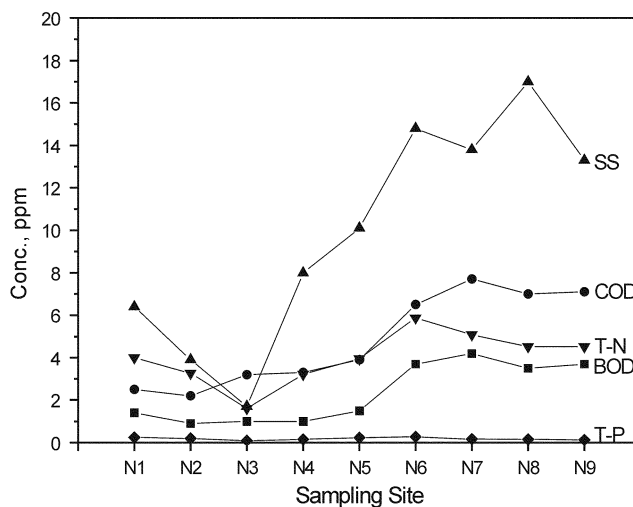
**Table 1.** Characteristics of the Major Rivers in Korea

River Name	Flow Length (Km)	Valley Area ( $\text{Km}^2$ )	Branch Number
Han River	7,256	26,018	705
Nakdong River	7,460	23,817	825
Keum River	3,742	9,810	503
Yongsan River	1,472	3,371	185



**Figure 3.** A river valley drawing and sampling sites in Nakdong river water system.

sampling sites in the Nakdong River water system. Figure 4 shows the average concentration of BOD, COD, SS, T-N and T-P by sampling sites in Nakdong river water system. Here, water quality is relatively good, but the N6 (Koryong) sampling site in the Kumho River, a city stream of Daegu,

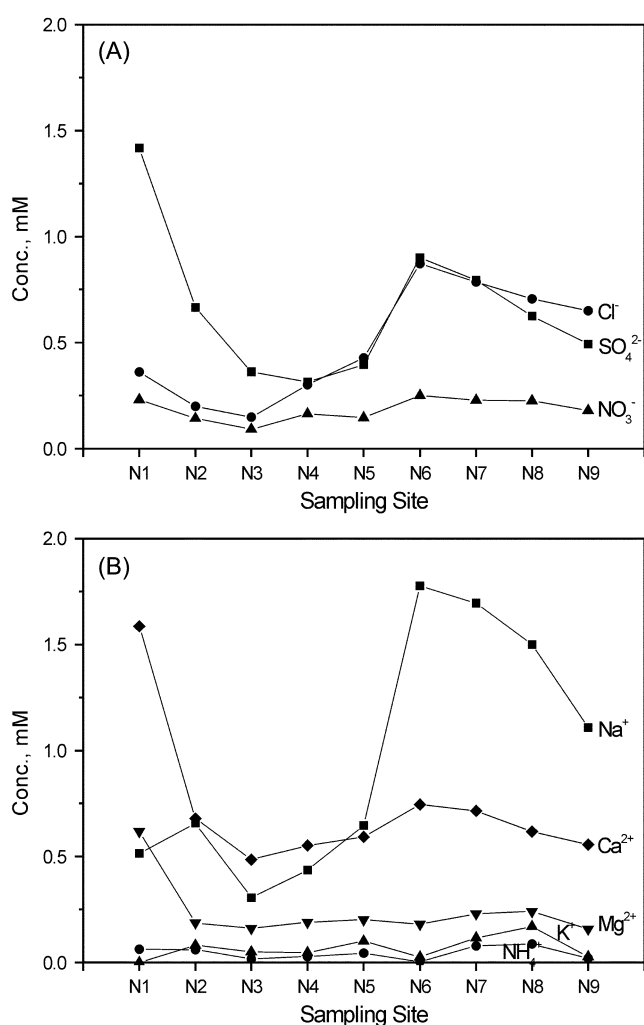


**Figure 4.** Average concentration of BOD, COD, SS, T-N and T-P by sampling sites in Nakdong river water system.

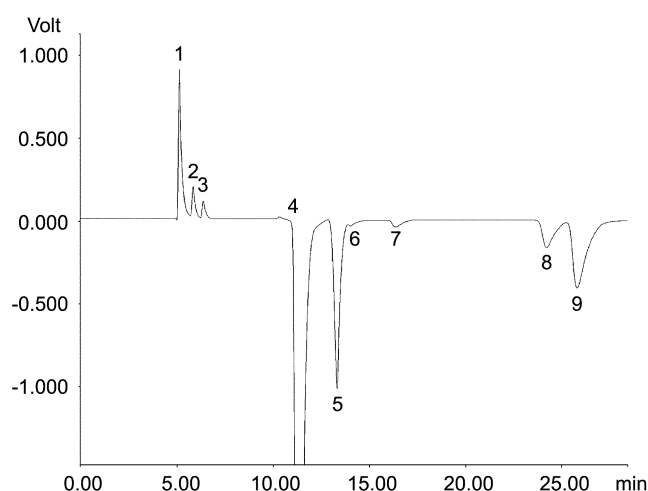
**Table 2.** Determination of Major Anions and Cations Concentration by Sampling Sites in Nakdong River Water System by IEC/CEC

Sampling Sites		Concentration (mM)								
		SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	H <sup>+</sup> (pH)
N1	Hwangji	1.418	0.361	0.230	0.514	0.063	ND	0.618	1.585	7.72
N2	Tosan	0.666	0.199	0.143	0.657	0.060	0.081	0.186	0.679	7.54
N3	Andong	0.362	0.148	0.091	0.306	0.017	0.050	0.161	0.485	7.21
N4	Sangju	0.314	0.301	0.164	0.435	0.028	0.046	0.190	0.551	7.43
N5	Waegwan	0.396	0.429	0.146	0.646	0.044	0.101	0.201	0.592	7.92
N6	Koryong	0.901	0.872	0.250	1.776	0.003	0.025	0.181	0.745	7.35
N7	Hapchon	0.794	0.786	0.228	1.694	0.079	0.116	0.229	0.714	7.44
N8	Hanam	0.625	0.706	0.226	1.500	0.087	0.169	0.241	0.617	7.73
N9	Kupo	0.493	0.650	0.180	1.108	0.020	0.027	0.157	0.556	7.27

ND = Not detected.

**Figure 5.** Concentration change of anions (A) and cations (B) according to sampling site in Nakdong river water system by using ion-exclusion/cation-exchange chromatography.

The pollution of the river was comprised of sewage and industrial waste water of Daegu. Table 2 lists the analytical results for major anions and cations, including H<sup>+</sup>, in sampling sites in the Nakdong River water system. Figure 6 shows the average concentration change of (A) anions (B)

**Figure 6.** Simultaneous ion-exclusion-CEC of anions and cations in river water of Nakdong river water system by elution with 1.4 mM sulfosalicylic acid/6 mM 18-crown-6-in water. Peaks: 1 = SO<sub>4</sub><sup>2-</sup>; 2 = Cl<sup>-</sup>; 3 = NO<sub>3</sub><sup>-</sup>; 4 = eluent dip; 5 = Na<sup>+</sup>; 6 = NH<sub>4</sub><sup>+</sup>; 7 = K<sup>+</sup>; 8 = Mg<sup>2+</sup>; 9 = Ca<sup>2+</sup>. Other chromatographic conditions are shown in Figure 1.

cations according to the sampling site in the Nakdong River water system by using ion-exclusion/cation-exchange chromatography. The pH values of these samples were in the range of 7.21-7.92. The anions and cations concentration of the N1 sampling site (Hwangji) was caused by waste water of a mine, and their concentrations were gradually lowered as the downstream. The concentration of waste water of the N6 sampling site (Koryong) was mainly due to general pollutant concentrations. As shown in Figure 6, the peak resolution among anions and cations was quite satisfactory. The simultaneous determination of major anions (SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>) and cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) in natural water obtained from the Nakdong River water system by IEC/CEC with a weakly acidic resin column was successfully performed.

## Conclusions

In this work, the simultaneous determination of anions and cations based on IEC/CEC was carried out. An excellent

separation and detection of anions and cations with a weakly acidic cation-exchange resin column was achieved in 25 min by elution with 1.4 mM sulfosalicylic acid/6 mM 18-crown-6 ether. The simultaneous determination of anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) in natural water obtained from the Nakdong River water system by IEC/CEC with a weakly acidic resin column was successfully performed. This result indicates that the IEC/CEC method was very useful for the simultaneous determination of anions and cations in natural water.

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