Development of a New Suppressor for the Ion Chromatography of Inorganic Cations

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This paper reports on a new suppressor that can be used in the ion chromatography (IC) of inorganic cations. The space in which the electrode is set on both sides of the device is separated into three cells using anion- and cation-exchange membranes. Each of the cells is packed with either an anion- or cation-exchange resin. Anions in the eluent and injected sample are removed by electrical regeneration, based on the electrokinetic phenomenon on both the surface of the ion-exchange resins and the membranes. The electrical conductivity of the suppressed eluent reaches a level similar to that of ultrapure water; therefore, a cation detection limit of sub-ppb order is achieved in IC using the device as a suppressor.

Keywords Ion chromatography, cation analysis, anion removal, suppressor

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Introduction

In 1975, Small and coworkers first introduced ion chromatography (IC), which is widely used in engineering, science, and other fields.¹⁻¹² Most ion chromatographs with an electrical conductivity detector (ECD) are equipped with a suppressor (such as a column-type suppressor, a micromembrane,⁶ or an electrolytically regenerated suppressor used as both a membrane and on ion-exchange resin⁶⁻¹³). The performance of the suppressor determines the detection limit of IC. Recently, these suppressor technologies have been applied to capillary IC using the capillary column as a separation column, and a suppressor for capillary IC has also been developed.¹⁴⁻¹⁷ A continuously and electrolytically regenerated packed-bed suppressor (known as Atlas) was made available by Dionex in 2001, which operates with high eluent concentrations, and has a very low dead volume.¹⁰ Other devices, called electrically regenerated ion suppression (ERIS)^{7,8} cells and the DS-Plus suppressor,¹¹ have been introduced by Alltech. These devices generate hydroxide and hydrogen ions (OH^- and H^+) by the electrolysis of water on the electrodes, and the generated OH^- acts as regeneration ions for neutralizing H^+ in an acidic eluent and converting the eluent to a low-conductivity solution. Both Atlas and ERIS have a recycle mode and an external mode. Nowadays, the recycle mode, which uses only one pump, is commonly adopted; waste fluid from the detector is used as the H_2O for pumping in the cathode and anode chambers. The external mode needs two pumps because external deionized water is used instead of waste fluid from the detector for high-sensitivity detection. The suppression capacity, which is the total amount of anions removed from the acidic eluent per

minute (1 mL/min), is higher in the external mode. However, because the H_2O pumped into the cathode chamber is contaminated with HCO_3^- (CO_3^{2-}) from CO_2 in the air, HCO_3^- (CO_3^{2-}) in the H_2O of the cathode chamber migrates from the cathode to the anode under an electric current (in this paper, anions migrating from cathode to the anode under an electric current are described as contamination anions). In this case, the contamination anions from the cathode to the anode are eluted from the suppressor by injected cations, which pass transversely across the contamination anions migrating from the cathode to the anode, and the signal intensity of the injected cations is decreased by them. Thus, to obtain higher detection sensitivity, it is necessary to decrease the contamination anions in the effluent from the suppressor.

This paper describes a new external-mode suppressor that can prevent the migration of contamination anions. A schematic of the device is shown in Fig. 1. The device is composed of three chambers separated by anion-exchange (AE) and cation-exchange (CE) membranes. The first is the anode chamber (AC); it contains the anode, AE resin packed into the remaining area, and pumped-in H_2O . The second is the regeneration chamber (RC), which is packed with AE resin and pumped-in acidic eluent. The third is the cathode chamber (CC); it contains the cathode, CE resin packed into the remaining area, and pump-in H_2O . The electrical conductivity of the acidic eluent is suppressed by the device on the basis of the following assumptions. First, anions existing in the RC and AC migrate to the anode by electrophoresis, which occurs on the surface of both the AE and CE phases. Second, cations existing in the CC migrate to the cathode; therefore, only anions from the injected sample and the acidic eluent pumped into the RC are removed. As discussed in this paper, the device has the following characteristics: (1) the suppression capacity is sufficient to continuously remove anions from the injected sample and the acidic eluent, (2) OH^- used to neutralize H^+ in the acidic eluent

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Fig. 1 Schematic of a device developed to suppress the electrical conductivity of acidic eluent. CC, cathode chamber; RC, regeneration chamber; AC, anode chamber; CE, cation exchange; AE, anion exchange.

is generated at points of contact between the AE and CE phases, (3) anion diffusion from the AC to the RC is prevented by pumping H_2O into the AE resin of the AC, (4) migration of contamination anions from the CC to the RC is prevented by the CE resin and the CC membrane, (5) cation migration from the RC to the CC is prevented by electro-osmotic flow caused by OH^- migration on the AE resin, (6) the electrical conductivity of the acidic eluent is suppressed to about the same as that of ultrapure water, and (7) a cation detection limit of sub-ppb order is achieved in IC for cation analysis.

Experimental

Device for suppressing electrical conductivity of acidic eluent used in IC for cation analysis

The developed device consists of a polyetheretherketone container (PEEK, 3 mm i.d., 46 mm length), which is separated by AE and CE membranes into the following three chambers. The CC (17 mm length), which is packed with CE resin (Amberlite IR120B, 0.6–0.8 mm, 2.0 meq/mL, Dow Chemical); the RC (12 mm length), which is packed with AE resin (Dowex 1X8, 200–400 mesh, 1.4 meq/mL, Dow Chemical); and the AC (17 mm length), which is filled with AE resin (Amberlite IRA402BL, 0.50–0.65 mm, 1.4 meq/mL, Dow Chemical). CMF was used as the CE membrane (Asahi Glass, Tokyo). AHA was used as the AE membrane (ASTOM, Tokyo). The device is shown in Fig. 1.

For a comparison with the developed device, two other devices were prepared: device CD1 (Fig. 2), composed of only an AE phase between the electrodes, and device CD2 (Fig. 3), with contact between the anode and AE membrane. In case of CD1, OH^- and H^+ , which act as regeneration ions, are generated on the electrodes; contamination anions migrate from the CC to the RC; and injected cations from the RC to the CC do not migrate. In the case of CD2, the anion concentration on the anode and the diffusion of anions from the AC to the RC are greater than those in the case of the developed device.

Acidic and basic solution systems

The acidic and basic solution systems are shown in Figs. 4 and 5, respectively. The acidic solution system was used to

Fig. 2 Schematic of CD1. CC, cathode chamber; RC, regeneration chamber; AC, anode chamber; AE, anion exchange.

Fig. 3 Schematic of CD2. CC, cathode chamber; RC, regeneration chamber; AC, anode chamber; CE, cation exchange; AE, anion exchange.

measure the suppression capacity and the effects of the AE resin and the H_2O pumped into the AC on anion removal. The basic solution system was used to measure the effect of the CE resin in the CC and the CE membrane on preventing contamination anion migration from the CC to the RC. The acidic system is composed of a pump (20 mM or 6 mM methanesulfonic acid (MSA) solution, 0.7 mL/min, CP-8020, Tosoh, Tokyo), a developed device used as an anion remover (AR) for removing anions from the acidic solution (*i.e.*, a power supply (0–50 mA, 0–100 V), Nichiri), and an ECD for measuring the electrical conductivity of the effluent from the AR (CM432, Nichiri). The basic system is composed of a pump (10 mM NaOH solution, 1.0 mL/min, CP-8020), a developed device used as an AR for removing trace anions from the basic solution (*i.e.*, a power supply (0–50 mA, 0–100 V), Nichiri), a cation remover (CR)¹² for removing cations from the basic solution (*i.e.*, a power supply (0–50 mA, 0–100 V), Nichiri), and an EDC for measuring the electrical conductivity of the effluent from the CR (CM432, Nichiri).

Ion chromatograph

An ion chromatograph (ICA2000, TOA DKK, Tokyo, Japan), into which both the developed device as a suppressor and a cation separation column (TSKgel superIC-CR, 150 × 4.6 mm i.d., 37°C, Tosoh) were installed, was used to measure the effect of the AE resin in the RC and the CE membrane on preventing the migration of injected cations from the RC to the CC, and the performance of the developed device as a suppressor in IC for cation analysis. The measurements were performed with a 2 mM MSA solution (about 500 $\mu\text{S cm}^{-1}$, 0.5–1 mL/min, 1.4 $\mu\text{eq/min}$) as an eluent. The developed device was operated

Fig. 4 Acidic solution system used in this study. P, pump; AR, anion remover (the developed device or CD2); R, recorder; ECD, electrical conductivity detector; RC, regeneration chamber; AC, anode chamber; AE, anion exchange.

Fig. 5 Basic solution system used in this study. P, pump; AR, anion remover (the developed device or CD1); CR, cation remover; ECD, electrical conductivity detector; CC, cathode chamber; RC, regeneration chamber; CE, cation exchange; AE, anion exchange.

Fig. 6 Suppression capacity. The measurement used the acidic solution system shown in Fig. 4.

at a constant electric current of 15 mA.

Results and Discussion

Suppression capacity

To measure the suppression capacity of the developed device, the electrical conductivity of the effluent from the device used as an AR in the acidic solution system shown in Fig. 4 was measured when an electric current between 0 and 40 mA was applied to the device. The acidic solution used was a 20 mM MSA solution (about $4876 \mu\text{S cm}^{-1}$). As can be seen from the graph of the suppression capacity shown in Fig. 6, the conductivity was found to decrease linearly with the electric current increasing from 0 to 15 mA, the conductivity of the MSA solution was reduced to $445 \mu\text{S cm}^{-1}$ at an electric current of 40 mA, and the suppression capacity of the device was about $10 \mu\text{eq/min}$ (1 mL/min). Since the eluent used for the TSKgel superIC-CR was 2 mM MSA solution, this device was confirmed to perform satisfactorily as a suppressor in the IC for cation analysis with on isocratic elution. In this case, the concentration of the anion eluted from the RC reached such dilute quantities that were not detected by the IC.

Effects of AE resin and H_2O pumped into AC on anion removal

To determine the effects of the AE resin and the H_2O pumped into the AC on anion removal, the electrical conductivity of the effluent from the developed device used as an AR in the acidic solution system shown in Fig. 4 was measured. For a comparison, device CD2 with contact between the anode and the AE membrane was prepared. The electrical conductivities of the effluent from the device and CD2 were measured under operation at a constant electric current of 10 mA. The acidic solution used was a 6 mM MSA solution (about $1500 \mu\text{S cm}^{-1}$). The conductivities of the developed device and CD2 were found to be 214 and $950 \mu\text{S cm}^{-1}$, respectively; the conductivity of the device was $736 \mu\text{S cm}^{-1}$ lower than that of CD2. In CD2, although H_2O was pumped into the AC, H_2O was not supplied at points of contact between the anode and the AE membrane because a large amount of O_2 gas was generated at these points. The concentration of MSA ions on the anode of CD2 was higher than that of the developed device. Therefore, the conductivity of CD2 was increased because of the increased diffusion of MSA ions from the AC to the RC. In the developed device, because sufficient H_2O on the anode was pumped to the AE resin between the AE membrane and the anode, the concentration

of MSA ions on the anode decreased. Therefore, the conductivity of the developed device was decreased as a result of the decreased diffusion of MSA ions from the AC to the RC.

Effect of CE resin in CC and CE membrane on preventing migration of contamination anions from CC to RC

The effect of the CE resin in the CC and the CE membrane on preventing the migration of contamination anions from the CC to the RC in the developed device was verified for the basic solution system shown in Fig. 5 under the following assumptions. For a comparison, device CD1 with contamination anions migrating from the CC to the RC was prepared. In device CD1, if the contamination anions migrated from the cathode to the anode by the electrokinetic phenomenon of electrophoresis and electro-osmotic flow, the contamination anions would be eluted from the RC by pumping a NaOH solution to the RC, and the contamination anions to be not removed by the CR could be measured by the ECD. The basic solution used was a 10 mM NaOH solution (about $2000 \mu\text{S cm}^{-1}$). These devices were operated at a constant electric current of 30 mA. The conductivity of the developed device was found to be $0.12 \mu\text{S cm}^{-1}$ lower than that of CD1. In CD1, the contamination anions migrated from the CC to the RC by electrophoresis and electro-osmotic flow, and the contamination anions were eluted from the CR by a NaOH solution pumped into the RC. In the developed device, both the CE resin and the membrane in the CC acted as an electrostatic barrier for the anions under the following speculations. First, because the surfaces of these cation exchangers were negatively charged, electro-osmotic flow on these cation exchangers occurred from the anode to the cathode. Second, on these cation exchangers, the velocity of the electro-osmotic flow was faster than the anion electrophoresis from the cathode to the anode. The migration of the contamination anions from the CC to the RC was prevented. Therefore, the conductivity of the developed device was less than that of CD1.

Location of the generation of OH^- acting as regeneration ions

The location at which OH^- , acting as regeneration ions, was generated in the developed device was determined under the following assumptions: OH^- and H^+ , acting as regeneration ions, are generated from H_2O , and if all of the H_2O is removed, the electric current between the electrodes will become zero. To determine the location of OH^- ion generation, the chamber having zero electric current was sought by stopping the solution flow to each of the three chambers (CC, RC, and AC). For a comparison, device CD1 with OH^- ion generation on the cathode was prepared. These devices were operated at a constant electric current of 30 mA. The electric current of the developed device was found to be zero when the acidic eluent flow to the RC was stopped; in contrast, the electric current of CD1 was zero when the flow of H_2O to the CC was stopped. In CD1, OH^- and H^+ , acting as regeneration ions, were generated by the electrolysis of water on the electrodes. To maintain electroneutrality between the electrodes, the anions absorbed on the anion exchanger and the OH^- were induced to migrate to the anode by electrophoresis and electro-osmotic flow. When the H_2O flow to the CC was stopped, the H_2O in the CC was removed by the electro-osmotic flow that occurred with the migration of the anions, and OH^- could not be generated on the cathode. Therefore, the electric current between the electrodes was zero. In the developed device, although OH^- and H^+ were also generated by the electrolysis of water on the electrodes, OH^- and H^+ were not induced to migrate to their counter electrodes because an electrostatic barrier for anions and cations had

formed on the surface of the ion-exchange resin in the CC and AC. This means that the OH^- and H^+ generated on the electrodes did not act as regeneration ions. OH^- and H^+ , which acted as regeneration ions, were generated at points of contact between the CE membrane and the AE resin through the dissociation of the aqueous solution. To maintain electroneutrality between the electrodes, the anions and cations adsorbed on the ion exchangers between the electrodes, as well as the OH^- and H^+ generated at the points of contact, were induced to migrate to their counter electrodes by electrophoresis and electro-osmotic flow. When the flow of acidic eluent to the RC was stopped, the H_2O in the RC was removed by the electro-osmotic flow that occurred with the migration of the anions and cations, and OH^- and H^+ could not be generated at the points of contact. Therefore, the electric current between the electrodes was zero.

Fig. 7 Effect of the anion-exchange resin in the regeneration chamber and cation-exchange membrane on preventing cation migration from the regeneration chamber to the cathode chamber. ●, Developed device; ▲, device CD1. Sample, 50 ppb Li^+ ; injection volume, 20 μL ; eluent, 2 mM MSA (0.5–1 mL/min); separation column, TSKgel superIC-CR (37°C, Tosoh).

Effect of AE resin in RC and CE membranes on preventing cation migration from RC to CC

The effect of the AE resin in the RC and the CE membranes on preventing cation migration from the RC to the CC in the developed device was verified under the following assumptions: if cation migration from the RC to the CC was caused by electrophoresis and electro-osmotic flow, the concentration of cations eluted from the RC would decrease with decreasing rate of acidic eluent flow in the RC. To determine whether the cations migrated from the RC to the CC, the concentration of Li^+ eluted from the RC was measured when the flow rate of the acidic eluent used in IC was 0.5–1 mL/min. For comparison, device CD1 without cation migration from the RC to the CC was prepared. As can be seen from the result shown in Fig. 7, the behaviors of both the developed device and CD1 were similar. This indicates that cation migration from the RC to the CC did not occur in the developed device. In the developed device, it was expected that the cations in the RC would be unable to reach the CE membrane owing to the electro-osmotic flow caused by OH^- migration on the AE resin. In addition, since the cations pumped into the RC were eluted from Outlet 2 without absorbing on the AE resin in the RC, because they were subjected to electrostatic repulsion on the AE resin in the RC, the velocity of cation elution by pumping was considerably higher than that of the cation electrophoresis to the CC. Therefore, the cations were eluted from the RC along with highly conductive OH^- , and were detected on top of the low-background eluent signal.

Performance of the developed device as a suppressor in IC for cation analysis

To evaluate the performance of the developed device as a suppressor in IC for cation analysis, various cations were determined by IC using the device. As can be seen from the chromatograms of standard inorganic cations shown in Fig. 8, the signal intensity of the water dip was lower with the developed device than without it. When the developed device was used as a suppressor, the reproducibility (CV, $n = 10$) of the peak height

Fig. 8 Chromatograms of standard inorganic cations. (a) With the developed device, (b) without the developed device. Samples, (1) Li^+ (50 ppb), (2) Na^+ (200 ppb), (3) NH_4^+ (200 ppb), (4) K^+ (500 ppb), (5) Mg^{2+} (500 ppb), (6) Ca^{2+} (500 ppb). Eluent, 2 mM MSA (0.7 mL/min). The other conditions are the same as those in Fig. 7.

Fig. 9 Calibration curve of Li^+ . ●, With the developed device; ○, without the developed device. Eluent, 2 mM MSA (0.7 mL/min). The other conditions are the same as those in Fig. 7.

for lithium, sodium, ammonium, potassium, magnesium, and calcium was found to be 2.94, 2.79, 1.66, 2.51, 0.77, and 0.42%, respectively. In addition, as can be seen from the calibration curve of Li^+ shown in Fig. 9, the signal intensity of the cations with the developed device was about half that without it. However, the noise intensity with the developed device was about 1/50 smaller than that without it. The detection limit of Li^+ with and without the developed device was 0.09 and 2 ppb, respectively ($S/N = 3$). The correlation coefficient of the calibration curve with and without the developed device between 0 and 500 ppb was 0.999 and 0.998, respectively. In addition, when the contamination anion was eluted by the cations, the signal intensity of the injected cations was decreased by the contamination anions, as described in the Introduction section. However, the signal intensity of the injected cations obtained by the developed device was similar to that obtained by CD1.

Although we have reported only the external mode results obtained with the device for the removal of eluent anions from an injected sample and the acidic eluent, as described in our previous paper,¹³ the device is also applicable to the removal of cations by simple manipulation, such as by changing the polarities of the electrode and the ion exchanger.

Conclusions

All experimental results described in this paper were consistent

with the mechanism described in the Introduction section. Desirable detection limits for injected cations and the size of the water dip were obtained in IC using this device. We are now developing a new type of recycle mode suppressor and generator, for which results will be published elsewhere.

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