

イオンクロマトグラフィーのための  
イオン交換樹脂を用いた  
サプレッサーと溶離液生成装置の開発

2016

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# Preface

The origins of modern ion chromatography (IC) were developed by Hamish Small and his coworkers at the Dow Chemical Company in 1975, when they introduced a novel ion-exchange chromatographic method for the separation and detection of the electrical conductivity of ionic species [1]. This method employed a low-capacity ion-exchange column for the separation of analyte ions in conjunction with a second high-capacity ion-exchange column and conductivity detector, which enabled continuous monitoring of the sample ions (anions or cations). The second column was called a “stripper” column (later termed a “suppressor”) and served to reduce the electrical conductivity of the eluent and increase the electrical conductivity of the sample ions. In the case of the analysis of anions, this was achieved by exchanging hydronium ions from the cation-exchange suppressor for co-cations (e.g., sodium) in the eluent, prior to the measurement of electrical conductivity. This resulted in the conversion of the effluent from the first column from high to low electrical conductivity (e.g., pure water or a weakly acidic solution), while increasing the electrical conductivity of the sample anion as a result of replacing the eluent co-cation with the more electrically conductive hydronium ion. The reverse situation occurred for the analysis of cations, where the suppressor was an anion-exchange column and the effluent from the first column was converted to low electrical conductivity (e.g., pure water or a weakly basic solution). The term “IC” was subsequently introduced when this technology was licensed to the Dionex Corporation for commercial development.

The introduction of IC provided a foundation for renewed interest in the determination of ionic solutes and prompted much investigation into the use of alternative separation and detection techniques for the liquid chromatographic analysis of inorganic compounds. In 1979, Fritz et al. showed that a suppressor was not essential for the sensitive detection of conductivity, provided that appropriate low-capacity stationary phases and eluents with low conductivity were used (later termed “non-suppressed IC”) [2, 3]. In addition, the separation of inorganic ions using traditional C18 reversed-phase columns was also being studied at about the same time [4]. Since that time, a considerable variety of separation and detection methods have been employed for the determination of ionic species.

In the meantime, the abbreviated term IC has become established as the generic term for the ion-exchange, ion-exclusion, and ion-pair chromatography methods included under high-performance liquid chromatography (HPLC). IC is currently considered to be an indispensable tool in a modern analytical laboratory for the separation of inorganic and organic substances that can decompose in water into

cations or anions [5–8]. Complex mixtures of anions or cations can usually be separated and quantitative amounts of the individual ions can be measured in a relatively short time.

The Thermo Scientific™ Dionex™ ion chromatograph, which has a suppressed electrical conductivity detector (ECD), is the most popular in the world and is equipped with an eluent generator to adjust the eluent concentration in-line and an electrolytically regenerated suppressor to remove ions (cations and anions) from the eluent. Otherwise, in a case where carbonate buffer instead of hydroxide solution is used as the eluent, the Metrohm ion chromatograph with a suppressed ECD is also popular for the analysis of anions; this is equipped with a CO<sub>2</sub> remover, which is installed between the column-type suppressor and detector to remove CO<sub>2</sub> gas that is contained in the effluent from the suppressor. These ion chromatographs are a superb way to determine ions present at concentrations down to at least the range of low parts per billion ( $\mu\text{g}/\text{kg}$ ). However, they are highly expensive and their components (suppressor, eluent generator, and CO<sub>2</sub> remover) are not available separately. In addition, these technologies are patent-protected.

This study aims to develop the following new devices as components for ion chromatographs. The operational mechanisms of these components are based on an electrokinetic phenomenon on the surfaces of both the ion-exchange resins and the membranes, with at least one boundary composed of an anion- and a cation-exchanger between the electrodes. The first is an in-line eluent generator that can tolerate high pressures and prepare a high-purity eluent that does not contain gases (H<sub>2</sub> or O<sub>2</sub>) produced by electrolysis of water at the electrodes or ionic impurities [9]. The second is an in-line electrolytically regenerated suppressor that can tolerate high pressures, convert the effluent from the separation column from high to low electrical conductivity (e.g., pure water or weakly acidic or basic solutions) and increase the electrical conductivity of the sample ions as a result of replacing the counter ion of the analyte ions by a more electrically conductive ion (hydronium or hydroxide ion) [10–12]. In addition, a CO<sub>2</sub> remover has also been developed as a component for ion chromatographs that are used for the analysis of anions with carbonate buffer as an eluent. CO<sub>2</sub> that is contained in the suppressor effluent can be removed by the CO<sub>2</sub> remover, which is based on diffusion of the CO<sub>2</sub> associated with a difference in its partial pressure [13]. IC with these components is a superb way to determine ions present at concentrations down to ppb level. Chapters 1–5 describe these components in detail.

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# Acknowledgments

Foremost, the author would like to thank his advisor, Prof. Shigeo Yamazaki, Okayama University of Science, for providing him with the opportunity to complete his Ph.D. thesis at Okayama University of Science as an external student. The author is also grateful to Prof. Keiitsu Saito, Kobe University, Prof. Takashi Yokoyama, Prof. Junichi Odo and Prof. Yuko Sugiyama, Okayama University of Science for their comments on this report. The author would like to express sincere thanks to Corporate Auditor, Dr. Yuji Higo, Mizuo Ishii, Noboru Maruyama, Nichiri MFG. CO. LTD., for their continuing interest and encouragement. Finally, the author thanks all members of his laboratory for their various supports.

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# Chapter 1

## Suppressor for Ion Chromatography of Anion Analysis

### 1.1 Introduction

The term “ ion chromatography ” (IC) was coined by Small, Stevens, and Baumann in 1975 when they first described a novel ion-exchange chromatographic method for the separation and the electrical conductivity detection of ionic species [1]. In the case of the analysis of anions, this method employed a low-capacity anion-exchange (AE) column for the separation of sample anions, in conjunction with a second high-capacity cation-exchange (CE) column and an electrical conductivity detector (ECD), which enabled continuous monitoring of the anions. The second column (later termed a suppressor) served to reduce the electrical conductivity of the eluent and increase the electrical conductivity of the sample anions. This was achieved by exchanging hydronium ions from the CE suppressor for co-cations (e.g., sodium) in the basic eluent, prior to the measurement of electrical conductivity. This resulted in the conversion of the effluent from the first column into pure water (or a weakly acidic solution), which has very low electrical conductivity, while increasing the electrical conductivity of the sample anion as a result of replacing the co-cation by the more electrically conductive hydronium ion.

The most important field of application today for anion chromatography is the routine investigation of aqueous systems; this is of vital importance in the analysis of drinking water [2–4]. IC is also used for the analysis of the elemental species in anionic elements or complexes; this is mainly for solving problems of environmental relevance. The third important field of application for anion chromatography is the ultra-trace analysis of ultrapure process chemicals, which is chiefly required in the semiconductor industry. The suppressor technique has grown in use at a phenomenal rate. The suppressors currently used in IC are columns [1], micro-membranes [5–7], and electrolytically regenerated packed-bed suppressors [8–12]; they are important in that they determine the detection limit in IC. The Thermo Scientific™ Dionex™ ion chromatograph, which has a suppressed ECD, is the

most popular in the world and is equipped with an electrolytically regenerated suppressor. This device generates hydroxide and hydrogen ions ( $\text{OH}^-$  and  $\text{H}^+$ ) by the electrolysis of water at the electrodes, and the generated  $\text{H}^+$  ions act as regeneration ions for neutralizing  $\text{OH}^-$  ions in a hydroxide eluent and converting the eluent into a low-conductivity solution. The suppressor in the Dionex has a recycle mode and an external mode; IC in the recycle mode is based on a single-pump system using waste fluid from the detector, whereas the external mode is based on a double-pump system using external deionized water. The suppression capacity, which is the total amount of cations removed from the basic eluent per minute (1 mL/min), is higher in the external mode. However, the recycle mode using waste fluid from the detector is commonly adopted.

This study aims to develop a new recycle-mode suppressor [13, 14], which has high suppression capacity. The device is shown schematically in Fig. 1.1. The container of the device has three compartments filled with ion-exchange resins that are isolated from each other by an AE and a CE membrane, and electrodes are installed at both ends of the container. Each of the compartments is packed with either AE or CE resins. Cations in the effluent from the separation column are removed by electrical regeneration, which is based on an electrokinetic phenomenon on the surfaces of both the ion-exchange resins and the membranes. When a constant current is applied between the electrodes, a boundary (B) serves as a place for the generation of  $\text{H}^+$  ( $\text{D}_\text{H}$ ) and  $\text{OH}^-$  ( $\text{D}_\text{OH}$ ) by the dissociation of water present at B without the electrolysis of water at the electrodes. Therefore, we anticipate that the position where cations are removed is separate from the position where water is electrolyzed; subsequently, a solution containing no gases or cations will be eluted and thus the electrical conductivity of the effluent will reach a level that is similar to that of ultrapure water. This paper describes the introduction of the device that has been developed with B between the electrodes.

## 1.2 Experimental

### 1.2.1 Device for removing cations from the sample and the eluent

The developed device consists of a polyetheretherketone (PEEK) container in which an ion exchanger and two platinum electrodes are installed.

As shown in Fig. 1.1, it is separated into cathode compartment (CC), regeneration compartment (RC) and anode compartment (AC) by an AE and a CE membrane. Each of the compartments is packed with either AE or CE resin. The AC is packed with AE resin (Amberlite IRA402BL, 0.5–0.65 mm, 1.4 meq/mL, Dow Chemical), the RC are packed with CE resin (Dowex 50X8, 200, 2.0 meq/mL, Dow Chemical), and the CC are packed with CE resin (Amberlite IR120B, 0.6–0.8 mm, 2.0 meq/mL, Dow Chemical). CMF was used as the CE membrane (Asahi Glass, Tokyo). AHA was used as the AE membrane (ASTOM, Tokyo). The Inlet1, Inlet2, and Inlet3 were connected to Pump1 (tubing pump, 1 mL/min of the flow rate is controlled by a home-made flow control driver), Pump2 (0.75–0.8 mL/min,

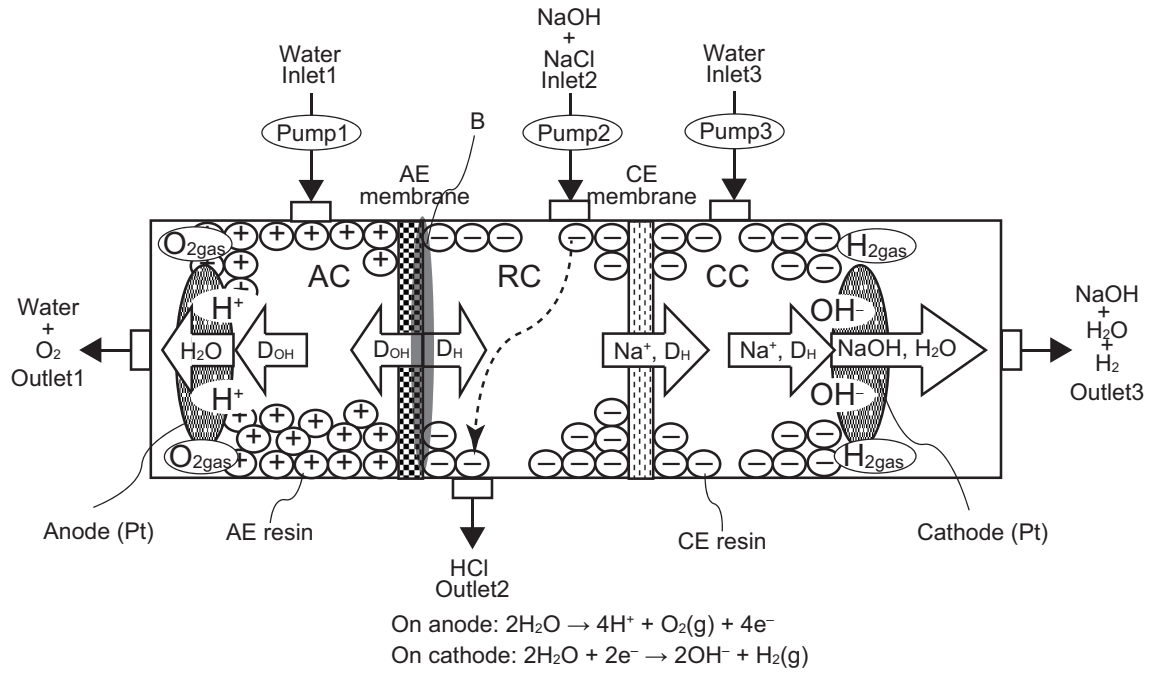


Figure 1.1: Schematic of the developed device. Reaction at B:  $\text{H}_2\text{O} \longrightarrow \text{H}^+(\text{D}_\text{H}) + \text{OH}^-(\text{D}_\text{OH})$

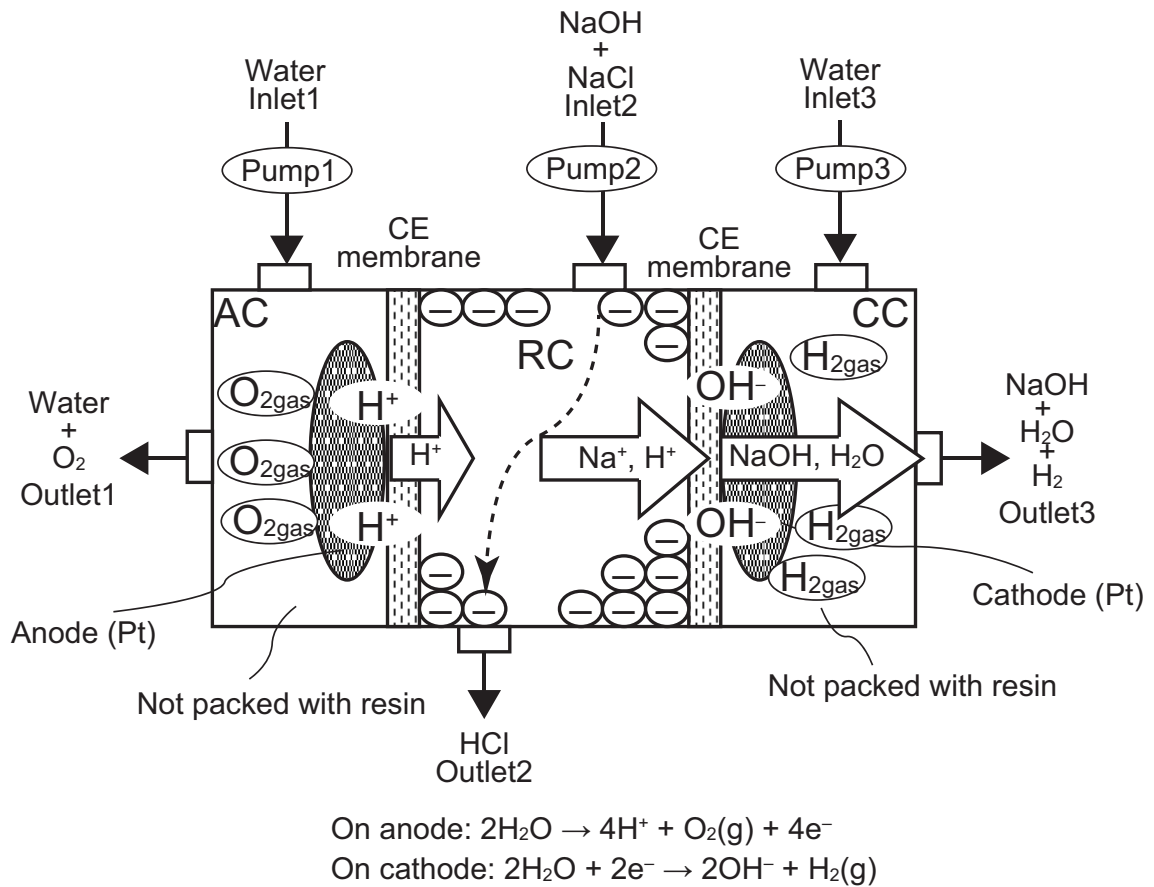


Figure 1.2: Schematic diagram of the CD.

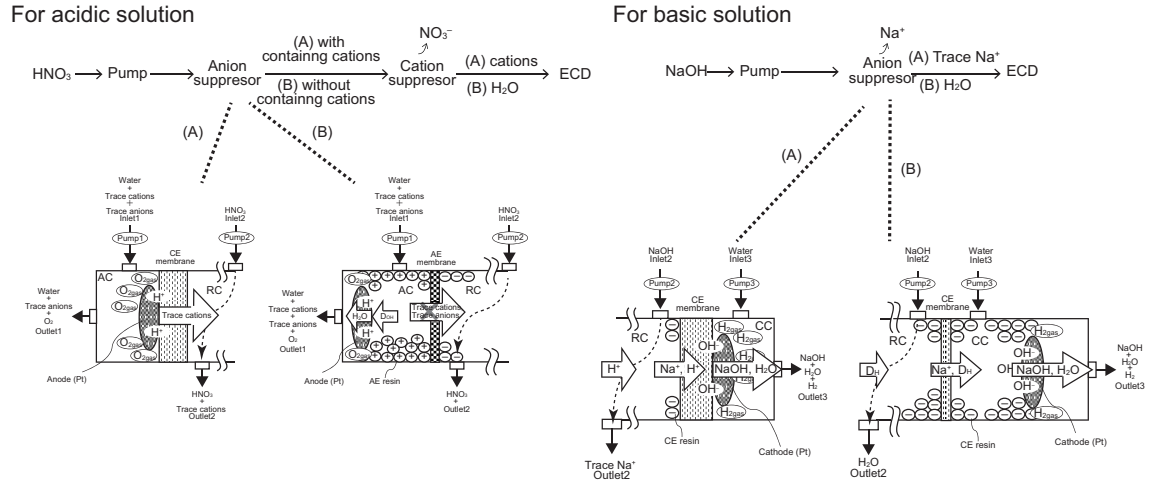


Figure 1.3: Schematic diagram of the system used in this work: (A) the CD, (B) the developed device.

DP-8020, Tosoh, Tokyo, Japan), and Pump3 (tubing pump, 1 mL/min of the flow rate was controlled by a home-made flow control driver), respectively. Deionized water (containing trace cations and anions) was pumped into Inlet1 and Inlet3. Electrolyte solution was pumped into Inlet2. The cations contained in the effluent from the separation column were removed.

A diagram of the comparing devices (CD) [3] prepared to confirm the proposed mechanisms of the developed device is shown in Fig. 1.2. the CD consists of only a cation exchanger between the electrodes.

## 1.2.2 Apparatus

The system used in this work is shown in Fig. 1.3. We assembled using a pump (Pump2 shown in Fig. 1.1 and .2), a suppressor for cation analysis (iSC8010 [13,14], Nichiri, Chiba, Japan), an suppressor for anion analysis (the developed device) and an electrical conductivity detector (ECD, CM432, Nichiri).

## 1.3 Results and Discussion

### 1.3.1 Generation position of $D_H$ and $D_{OH}$

We anticipate that  $H^+(D_H)$  and  $OH^-(D_{OH})$  are generated by the dissociation of water existing at B of the developed device. The generation positions of  $D_H$ , and  $D_{OH}$  were determined. If the water is not pumped into the RC of the developed device, the water in the RC is consumed by generation of  $D_H$  and  $D_{OH}$ . Thus, the electrical current through the electrodes will be decreased without the replenishment of  $D_H$ , and  $D_{OH}$ . Variation of the electrical current through the electrodes when the pure water is not pumping into the RC under a constant voltage output 35 V is shown in Fig. 1.4. We observe that the electrical current is decreased when the water is not pumped into the RC. The result illustrates that the generation of  $D_H$ , and  $D_{OH}$

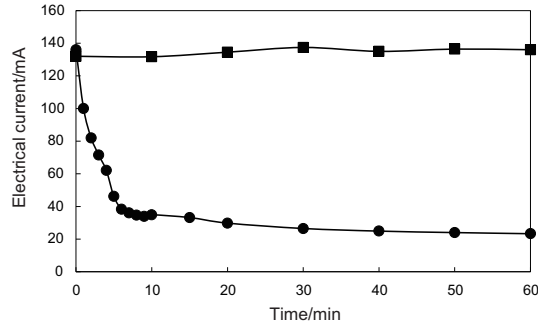


Figure 1.4: Electrical current variation passing through between the electrodes with or without pumping water to the RC of the developed device under a constant voltage output 35 V. without pumping water to the RC, with pumping water to the RC, the AC and the CC.

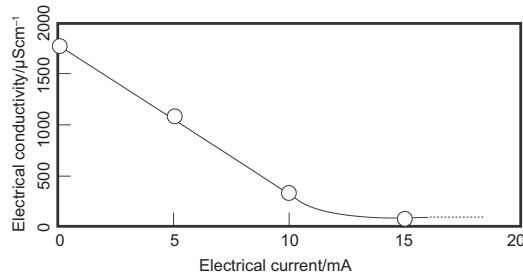


Figure 1.5: Relationship between the electrical current amount and the cation removal amount.

is decreased by consumption of water in the RC, and so  $D_H$ , and  $D_{OH}$  are generated by the dissociation of water existing at B.

### 1.3.2 Relationship between the electrical current and the amount of removal cations

To confirm the relationship between the electrical current and the amount of the cations removal, the electrical conductivity of the effluent from the developed device was measured when the developed device was operated at a constant electrical current of 0, 5 and 15 mA. The measurement was carried out using the system for basicity as shown in Fig. 1.3. The results are given in Fig. 1.5. We observe that the electrical conductivity of a prepared sodium hydroxide solution (about  $1700 \mu\text{S}/\text{cm}$ ) is decreased in proportion to the electrical current when the applied electrical current is increased from 0 to 15 mA, and decreased to less than  $1 \mu\text{S}/\text{cm}$  when the applied electrical current is 20 mA. These results mean that sodium ion ( $\text{Na}^+$ ) of the sodium hydroxide solution is sufficiently removed from the sodium hydroxide solution by the developed.

### 1.3.3 Function of water stream supplied to the CC packed with the CE resin

The function of water stream supplied to the CC packed with the CE resin was determined. The measurement was carried out using the system for basicity shown in Fig. 1.3. The electrical conductivities of the device developed and the CD were measured, when these devices were operated at a constant electrical current of 10 mA. We found that the electrical conductivity of a sodium hydroxide solution (1500  $\mu\text{S}/\text{cm}$ ) was 69  $\mu\text{S}/\text{cm}$  by the developed device, and was 469  $\mu\text{S}/\text{cm}$  by the CD. For the CD, although a stream of water was supplied in the CC, because a larger amount of  $\text{H}_2$  gas on the cathode was generated, the stream of water could not be supplied to a point of contact between the cathode and the CE membrane. Therefore, the amount of  $\text{Na}^+$  on the cathode would markedly increase, and so the  $\text{Na}^+$  will move to the RC with the concentration diffusion.

For the developed device, because a stream of water was supplied in the CC packed with the CE resin between the CE membrane and the cathode, the amount of  $\text{Na}^+$  on the cathode will decrease, and so the  $\text{Na}^+$  will not move to the RC with the concentration diffusion. Therefore, the effluent electrical conductivity of the developed device is lower than that of the CD.

### 1.3.4 Function of the AE resin and the membrane in the AC

The function of the AE resin and the membrane in the AC was determined. The measurement was carried out using the system for acidity shown in Fig. 1.3. If trace cations contained in water pumped into the AC are migrated from the AC to the RC by the electrokinetic phenomenon of electrophoresis and electro-osmotic flow, the cations is eluted from the RC by pumping a 2 mM  $\text{HNO}_3$  (ca. 600  $\mu\text{S}/\text{cm}$ ) solution to the RC. Because the cations are not removed by the cation suppressor, the cations will be measured by the ECD. The electrical conductivities of the effluent from the cation suppressor when the developed device and the CD were used under a constant electrical current of 40 mA were measured. We found that the electrical conductivity of the effluent from the cation suppressor when the developed device was used was 5  $\mu\text{S}/\text{cm}$  lower than when that when the CD was used.

The result illustrate that the cations are not migrated from the AC to the RC when the developed device is used, and are migrated from the AC to the RC when the CD is used. The result means that the cations migration from the AC to the RC is prevented by the electrostatic barrier effect for cations of the AE resin and the membrane in the AC.

## 1.4 Conclusions

All experimental results described in this paper were consistent with the mechanism described in the Introduction. The developed device's container has three

compartments (AC, RC and CC) separated by AE and a CE membrane. The RC is equipped with one boundary of B. Because the cation removal position is separated from the water electrolysis position, a solution containing no gases and impurity cations can be subsequently eluted from the RC. In addition, the device has a very low dead volume and high capacity for suppressing the electrical conductivity of the separation column effluent. Therefore, the device can suppress the electrical conductivity of the effluent to a level similar to that of ultrapure water under the recycle mode condition.

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## Chapter 2

# Hydroxide Solution Generator for Ion Chromatography of Anion Analysis

### 2.1 Introduction

Hydroxide solutions are used as carriers, eluents, and diluting solutions in analysis techniques such as HPLC, LC, and titration. They are also used in the fields of science and engineering and have to be prepared and replenished by the user. The technique employed herein is illustrated with specific reference to the production of NaOH solutions. In conventional methods, better NaOH solutions can be made from 50% (w/w) NaOH solution stock. Keeping CO<sub>2</sub> out of purified NaOH solution over such a period is very difficult, time-consuming, and often tedious [1]. A NaOH solution contains varying amounts of dissolved CO<sub>3</sub><sup>2-</sup>; therefore, more automated methods of hydroxide solution preparation are desirable. Dasgupta et al. have pioneered the application of electrolytic methods to purify eluents for ion chromatography (IC) and electrically control their concentration. Two basic types of generators were described in 1991. The first was a single-membrane device that generated a NaOH solution stream containing H<sub>2</sub> gas generated by electrolysis of water on a cathode. H<sub>2</sub> gas that interferes with the analysis was removed by a membrane degasser. The second was a multiple-membrane device that generated a NaOH solution stream without containing H<sub>2</sub> gas. The challenge of these membrane-based devices was to withstand high pressures [2, 3]. Small et al. introduced a new concept called ion reflux, wherein eluent generation and suppression have been integrated into an automated and, in principle, perpetual form of IC [4–6]. Dionex introduced the EG40 eluent generator that generated pure KOH solution in line, which was based on the electrolysis of deionized water. The concentration of the KOH was controlled by the amount of current applied to the device. Gradients could be easily programmed because the relationship between the KOH concentration and applied current was linear [6, 7]. Although these devices (ion reflux and EG40) withstood high pressures because the KOH was prepared by a reaction of K<sup>+</sup> arriving at the cathode with OH<sup>-</sup> generated

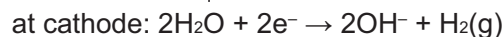
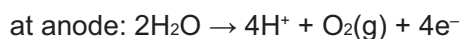
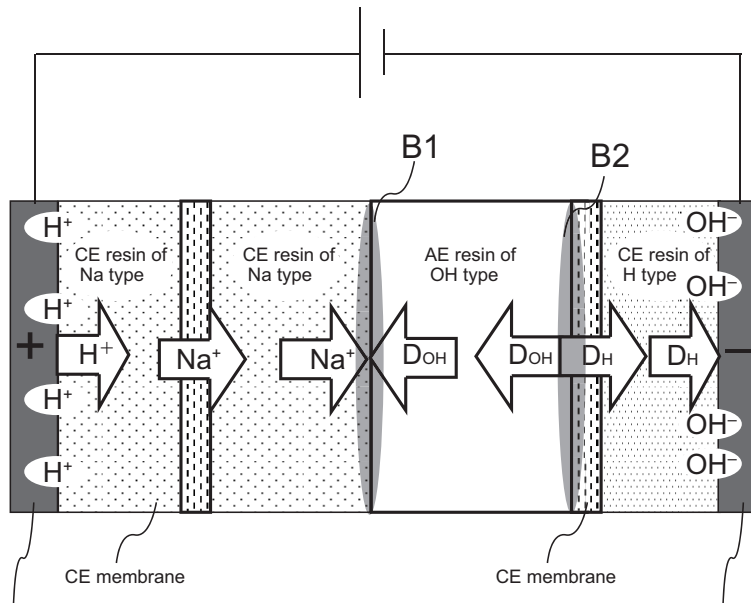


Figure 2.1: Schematic of the developed device. Reaction at B1:  $\text{Na}^+ + \text{OH}^- \rightarrow \text{NaOH}$ , reaction at B2:  $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ .

by electrolysis of water on the cathode, these devices prepared a KOH solution stream containing  $\text{H}_2$  gas generated by electrolysis of water on the cathode.  $\text{H}_2$  was removed by a membrane degasser developed for HPLC.

This study aims to develop a new device that can tolerate high pressures and prepare a high-purity hydroxide solution in line that does not contain gases ( $\text{H}_2$  or  $\text{O}_2$ ) produced by electrolysis of water on the electrodes and impurity anions [8]. Our working hypothesis is schematically shown in Fig. 2.1.

The device's container has three compartments filled with ion-exchange resins that are isolated from each other by two cation-exchange(CE) membranes, and an electrode is installed at both ends of the container. A center compartment has a space with two boundaries composed by sandwiching an anion-exchange(AE) layer between two CE layers and membrane. When a constant current is applied between the electrodes, one boundary (B1) serves as a place for  $\text{Na}^+$  to react with  $\text{OH}^-$ , while another boundary (B2) serves as a place for  $\text{H}^+$  ( $\text{D}_\text{H}$ ) and  $\text{OH}^-$  ( $\text{D}_\text{OH}$ ) to generate by the dissociation of the water existing at B2 without the electrolysis of water on the electrodes. Therefore, we anticipate that the NaOH solution generation position is separated from the water electrolysis position; subsequently, a high-purity hydroxide solution containing no gases or impurity anions will be generated. This paper describes the introduction and the mechanism of the developed device with a space that has two boundaries. Moreover, the concentration of the NaOH solution generated by the variation of an applied current (0–100 mA) is 0.01–60 mM.

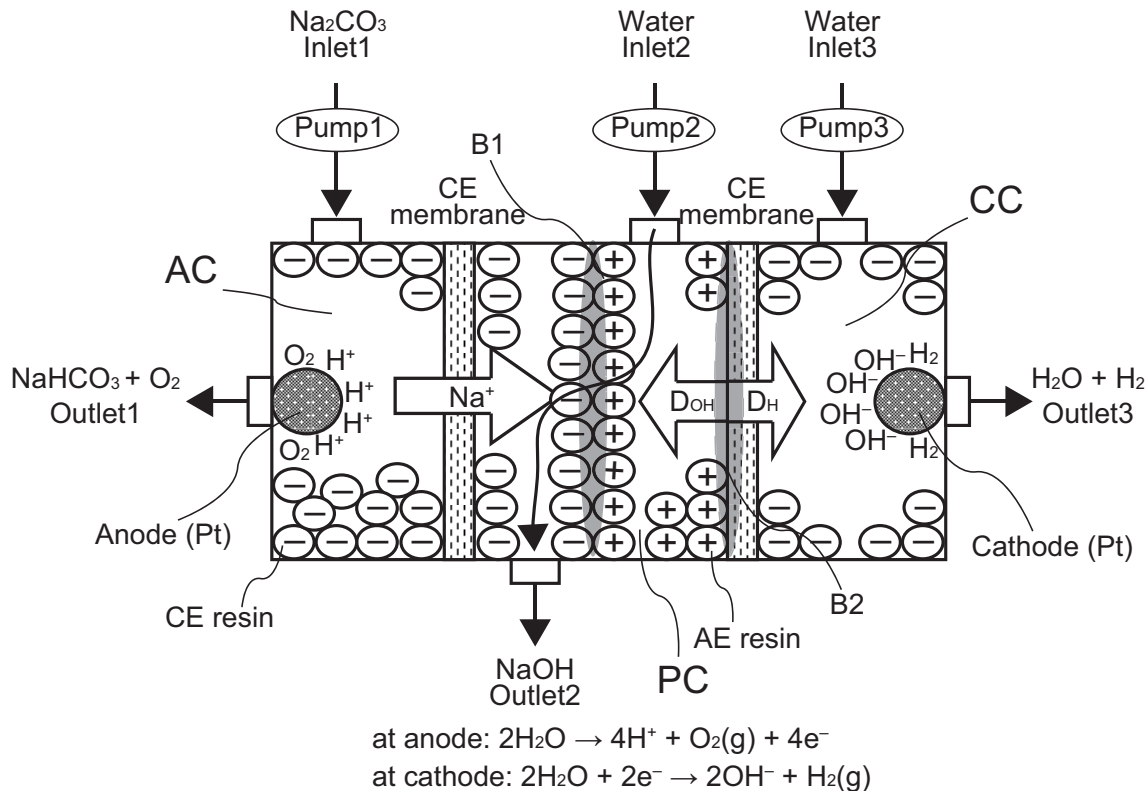


Figure 2.2: Schematic of the developed device

## 2.2 Materials and Methods

### 2.2.1 Developed device

A diagram of the developed device is shown in Fig. 2.2. The device's container has three compartments that are isolated from each other by two CE membranes (12 mm, CMF, Asahi Glass, Tokyo). The cathode compartment (CC length: 15 mm) is packed with CE resin (Amberlite IR120B, 0.6–0.8 mm,  $\geq 2.0$  meq/mL, Dow Chemical); the preparation compartment (PC length: 15 mm) comprising a cation and an anion exchanger phase. The cation exchanger phase contains CE resin (Dowex 5WX8, 200–400 mesh, 1.7 meq/mL, Dow Chemical). The anion exchanger phase contains AE resin (Dowex 1X8, 200–400 mesh, 1.2 meq/mL, Dow Chemical) and the anode compartment (AC, 15 mm length) is filled with CE resin (Amberlite IR120B). Inlet1, 2, and 3 were connected to Pump1 (tubing pump, 1 mL/min of the flow rate is controlled by a home-made flow control driver), 2 (1.3 mL/min, DP-8020, Tosoh, Tokyo, Japan), and 3 (tubing pump, 1 mL/min of the flow rate was controlled by a home-made flow control driver), respectively. 100 mM  $\text{Na}_2\text{CO}_3$  solution was pumped into Inlet1. Pure water was pumped into Inlet2 and 3 and the generated NaOH solution was then eluted from Outlet2.

A diagram of the comparing devices CD prepared to confirm the proposed mechanisms of the developed device is shown in Fig. 2.3, respectively. Because the CD is packed with the CE resin instead of the AE resin, boundaries consisting

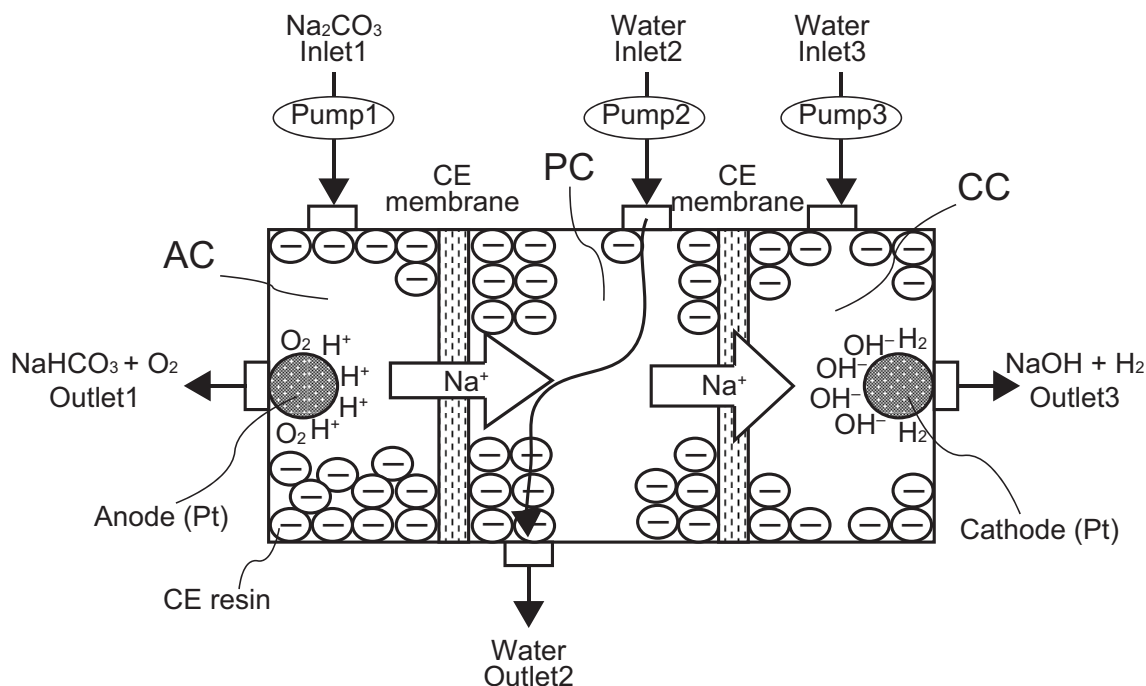


Figure 2.3: Schematic of the CD

of the cation exchanger and AE resin do not exist in the CD. Inlet1 was pumped with 100 mM  $\text{Na}_2\text{CO}_3$  solution. Inlet2 and 3 were pumped with pure water and the NaOH solution generated was then eluted from Outlet3.

### 2.2.2 Electrical conductivity measurement of NaOH solution generated by the developed device

Outlet2 of the developed device and Outlet3 of the CD were connected to an electrical conductivity detector (ECD, iCM8401, Nichiri) and the electrical conductivity of the effluent was then determined by the detector.

### 2.2.3 Ion chromatograph for qualitative analysis of the impurity anions contained in NaOH generated by the developed device

An ion chromatograph (ICA-2000) was equipped with a pump (1 mL/min, ICA-2000), an injector (20  $\mu\text{L}$ , ICA-2000), a separation column (TSKgel superIC-AZ, 150  $\times$  4.6 mm i.d., 40  $\mu\text{m}$ , Tosoh or IC-SA2, 250  $\times$  4 mm i.d., 40  $\mu\text{m}$ , Shimadzu, Kyoto, Japan), a suppressor (Chapter1, iSA8010 [9], Nichiri) and an ECD (ICA-2000). Effluent (ca.15 mM NaOH solution, 3236  $\mu\text{S}/\text{cm}$ , pH 11.98) from Outlet2 of the developed device was fed via a tee into the pump of the ECD and used as an eluent for IC. The injected sample was separated using the separation column,  $\text{Na}^+$  was removed from the eluent with aid of the suppressor, and the suppressor effluent was then determined by the ECD.

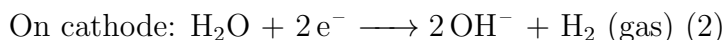
## 2.2.4 Mechanisms

Ion exchangers such as ion-exchange resins and membranes have mobile counter ions, making them good electrical conductors [10,11]. Consider these ion exchangers retained between the metal electrodes and the water pumped into it. If a DC potential is applied between the electrodes, the electric field will induce the positive counter ions to move toward the cathode and vice versa. In the developed device's case, the anodic oxidation of water produces  $H^+$  and  $O_2$  gases.



Because the AC is separated from the PC by the CE membrane, the  $O_2$  gas is eluted with  $Na_2CO_3$  solution passed from Inlet1 to Outlet1. Moreover,  $CO_3^{2-}$  contained in the  $Na_2CO_3$  solution is also eluted with the  $Na_2CO_3$  stream. The  $H^+$  sequentially migrates into the CE resin of the AC and the CE resin of PC, displacing the other  $H^+$  and, in turn,  $Na^+$  toward the cathode.

The PC's boundaries B1 and B2 are between the CE and the AE resin, and the AE resin and the CE membrane, respectively. Because the AE resin has a positive charged stationary phase, cations such as  $H^+$  and  $Na^+$  will collect and be concentrated at B1. We anticipate that  $D_H$  and  $D_{OH}$  will be generated by the dissociation of water existing at B2.  $D_H$  and  $D_{OH}$  migrate toward the cathode and B1, respectively. If the water is depleted in the AC and/or the PC, the electrical current will not pass through the electrodes without the replenishment of  $H^+$ ,  $D_H$  and  $D_{OH}$ . This means that the water has to be pumped into the AC and the PC to maintain a constant electrical current through the electrodes. Because the PC is separated from the AC and the CC by two CE membranes, the  $Na^+$  concentrated at B1 reacts with  $D_{OH}$  and is eluted as NaOH solution with the water passing from Inlet2 to Outlet2 across B1. The cathodic reduction of water produces  $H_2$  gas and an equivalent number of  $OH^-$  as companions for the  $D_H$  arriving at the cathode.



Because the CC is separated from the PC by the CE membrane, the  $H_2$  gas is eluted with pure water passed from Inlet3 to Outlet3. Furthermore, impurity cations and anions contained in the water are also eluted with the water stream.

The NaOH solution generation position of the developed device is separated from the water electrolysis position; thus, the desired high-purity NaOH solution can be prepared in line.

## 2.3 Results and Discussion

### 2.3.1 Generation position of $H^+$ , $OH^-$ , $D_H$ and $D_{OH}$ needed to maintain a constant electrical current through the electrodes

The generation positions of  $H^+$ ,  $OH^-$ ,  $D_H$  and  $D_{OH}$  were determined. We anticipate that  $H^+$  and  $OH^-$  are generated by the electrolysis of water on the electrodes, and  $D_H$  and  $D_{OH}$  are generated by the dissociation of water existing at B2. If the water is not pumped into the PC of the developed device, the water in the PC is consumed by generation of  $D_H$  and  $D_{OH}$ . Thus, the current through the electrodes will be decreased without the replenishment of  $D_H$  and  $D_{OH}$ . Moreover, if the water is not pumped into the AC or the CC, the water in the AC or the CC is consumed by electrolysis. Thus, the current through the electrodes will be decreased without the replenishment of  $H^+$ ,  $OH^-$ . Variation of the current through the electrodes when the pure water is not pumping into one of three compartments (CC, PC, and AC) under a constant voltage output 40 V is shown in Fig. 2.4.

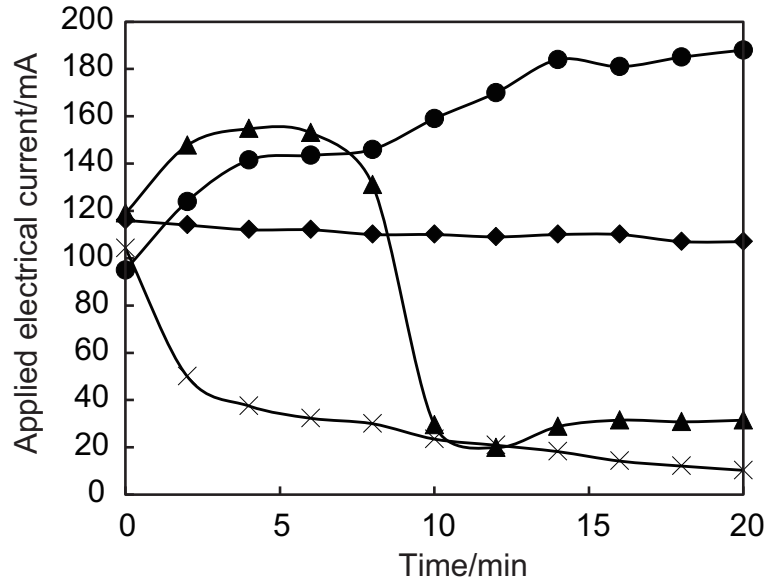


Figure 2.4: Variation of applied current passing through the electrodes when the water is pumped into one of three compartments (CC, PC, and AC) of the developed device under a constant voltage output 40 V.  $\bullet$  without pumping water to PC,  $\times$  without pumping water to the AC,  $\blacktriangle$  without pumping water to the CC,  $\blacklozenge$  with pumping water to the PC, the AC, and the CC.

In Fig. 2.4, we observe that current is decreased when the water is not pumped into the PC or the AC, and is not decreased in the case of the CC. The result exhibiting that current decreases when the water is not pumped into the AC and the PC illustrate that the generation of  $H^+$ ,  $D_H$  and  $D_{OH}$  is decreased by consumption of water in the PC and the AC. The cause for increased current

when the water is not pumped into the PC and the CC is unknown. The result exhibiting that the current decreases when the water is not pumped into the AC and the PC illustrates that the trace water is supplied on cathode by electro-osmotic flow from B2 to cathode; thus, the water in the CC is not consumed. Therefore, these results mean that  $H^+$  and  $OH^-$  are generated by the electrolysis of water on the electrodes, and that  $D_H$  and  $D_{OH}$  are generated by the dissociation of water existing at B2, respectively.

### 2.3.2 Separation of the NaOH solution generation position from the electrolysis position

To confirm whether the gases were contained in the NaOH solution prepared by the developed device and the CD, the electrical conductivity of effluent from these devices was measured. A well-known characteristic of the ECD is that a spike-like noise is measured when the gas enters the detection solution. The electrical conductivity of the NaOH solution ( $\sim 12.5$  mM,  $2809 \mu S/cm$ ) generated by these devices is shown in Fig. 2.5. We observe that the spike-like noise is not measured in the effluent of the developed device but that of the CD. This result illustrates that the gases is not contained in the NaOH solution generated by the developed device.

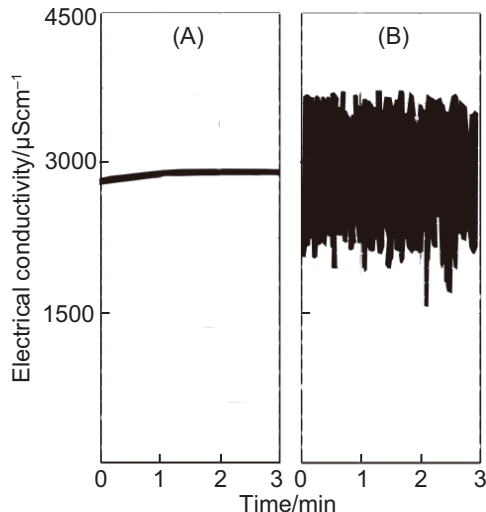


Figure 2.5: Electrical conductivity of NaOH solution generated by the developed device and the CD. (A) the developed device, (B) the CD.

In the next experiment, 1 mM  $HNO_3$  solution (at 1.1 mL/min) was pumped from Inlet2 to Outlet2 of the developed device and from Inlet3 to Outlet3 of the CD. It is well known that electrochemical reduction reaction is caused on the cathode under an electric field.  $NO_2^-$  should be produced by electrolysis of  $NO_3^-$  on the cathode. The results illustrates whether the generated NaOH solution is

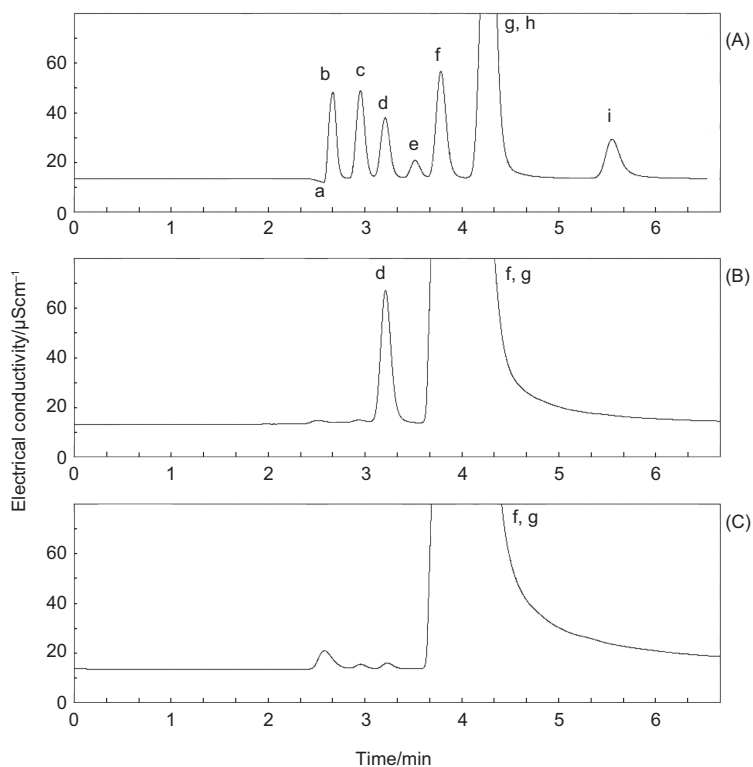


Figure 2.6: Chromatograms of solution generated by the developed device and the CD.; (A) standard inorganic anions, (a) water dip, (b)  $\text{F}^-$  (50ppb), (c)  $\text{Cl}^-$  (100ppb), (d)  $\text{NO}_2^-$  (150ppb), (e)  $\text{Br}^-$  (100ppb), (f)  $\text{NO}_3^-$  (300ppb), (g)  $\text{CO}_3^{2-}$  (unknown), (h)  $\text{SO}_4^{2-}$  (400ppb), (i)  $\text{PO}_4^{2-}$  (300ppb); (B) the CD; and (C) the developed device; separation column (TSKgel superIC-AZ).

electrolyzed on the cathode. Chromatograms of the effluent from Outlet2 and 3 determined by the IC for anion analysis are shown in Fig. 2.6. We observe that the peak of  $\text{NO}_2^-$  is not measured in the effluent of the developed device but that of the CD. Because the NaOH solution generated by the developed device is not passed through the cathode,  $\text{NO}_2^-$  is not contained in the NaOH solution. These results mean that the developed device can separate the NaOH solution generation position from the water electrolysis position and thus generate the desired NaOH solution.

### 2.3.3 Performance of the developed device: purity of the NaOH solution generated by the developed device

To estimate the developed device's performance, the concentration of impurity anions containing the NaOH solution generated by the developed device was determined. In the experiment, ultra-pure water is pumped into the developed device's PC, A chromatogram of the NaOH solution ( $\sim 15\text{ mM}$ ,  $3236\ \mu\text{S}/\text{cm}$ , pH 11.98) prepared by the developed device is show in Fig. 2.7. For a comparison with the developed device, the NaOH solution prepared by the conventional method



(15 mM NaOH prepared from 50% (w/w) NaOH solution stock,  $3465 \mu\text{S}/\text{cm}$ , pH 11.9) was also measured. In Fig. 2.7, we observe that anions are not contained in the NaOH prepared by the developed device and are contained in the NaOH prepared by the conventional method. The result illustrates that the anions are not migrated from the AC and the CC to the PC of the developed device, i.e., if ultra-pure water is pumped into the PC of the developed device, the developed device can generate the desired NaOH solution.

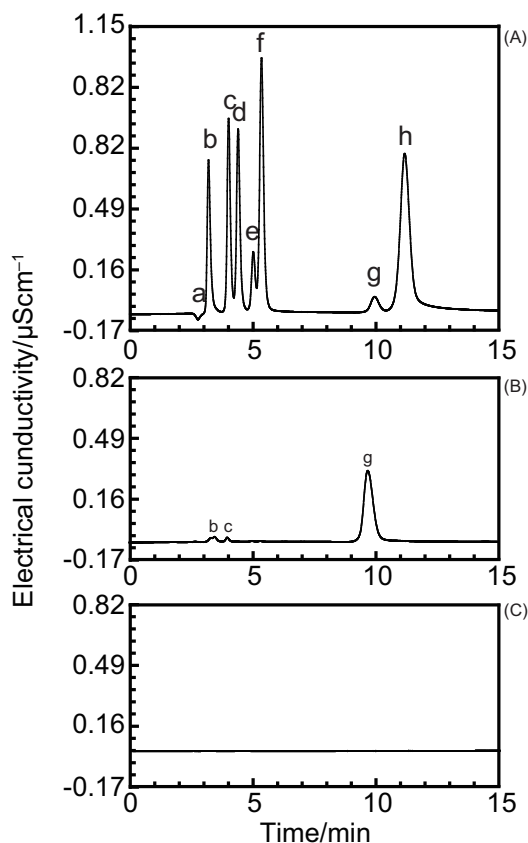


Figure 2.7: Anions in the NaOH solution generated by the developed device. (A) standard inorganic anions, (a) water dip, (b)  $\text{F}^-$  (0.5ppm), (c)  $\text{Cl}^-$  (1ppm), (d)  $\text{NO}_2^-$  (1.5ppm), (e)  $\text{Br}^-$  (1ppm), (f)  $\text{NO}_3^-$  (3ppm), (g)  $\text{CO}_3^{2-}$  (unknown), (h)  $\text{SO}_4^{2-}$  (4ppm); (B) 15 mM NaOH solution prepared from 50% (w/w) NaOH solution stock, (b)  $\text{F}^-$  (unknown), (c)  $\text{Cl}^-$  (unknown), (g)  $\text{CO}_3^{2-}$  (unknown); (C) approximately 15 mM NaOH solution generated by the developed device, separation column (IC-SA2).

### 2.3.4 Concentration of the NaOH solution generated by the developed device

Concentration of the NaOH solution generated by the developed device was determined. A well-known characteristic of the ECD is that the concentration of NaOH solution can be estimated from the obtained electrical conductivity value [12].

Variation of the electrical conductivity of the NaOH solution generated by the developed device under the various applied currents is shown in Fig. 2.8. We observe high linearity between current and the concentration of generated NaOH solution. The result corresponds to a linear relationship ( $r = 0.999$ ) with a slope of  $0.624 \text{ mM/mA}$ . In another experiment, the current applied between the electrodes was  $40 \text{ mA}$ , the electrical conductivity of NaOH solution was  $5646 \mu\text{S/cm}$ , corresponding to a NaOH concentration of  $25.26 \text{ mM}$ . Moreover, the current was then reduced to  $20 \text{ mA}$  and the generated NaOH solution concentration was found to be  $12.57 \text{ mM}$ . This result confirms the linear dependence of the NaOH solution concentration on current applied between the electrodes and illustrates the ability to control the concentration of the NaOH solution produced by the variation of applied current passing through the electrodes.

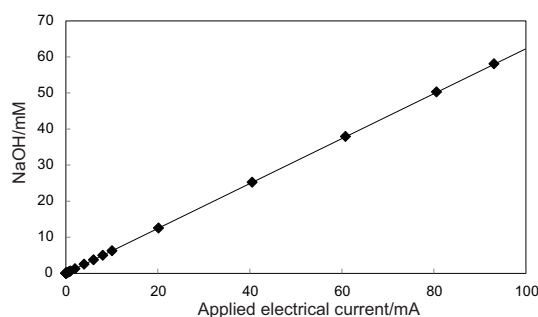


Figure 2.8: Specific concentration of the NaOH solution generated by the developed device as a function of the current applied to it.

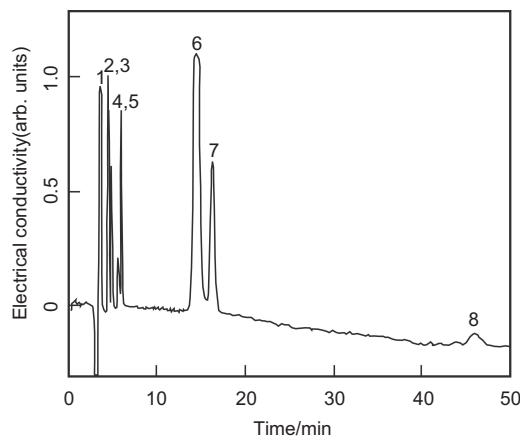


Figure 2.9: Chromatogram of standard inorganic anions. Samples: 1,  $\text{F}^-$  (5ppb); 2,  $\text{Cl}^-$  (10ppb); 3,  $\text{NO}_2^-$  (15ppb); 4,  $\text{Br}^-$  (10ppb); 5,  $\text{NO}_3^-$  (30ppb); 6,  $\text{SO}_4^{2-}$  (unknown); 7,  $\text{SO}_4^{2-}$  (40ppb); 8,  $\text{PO}_4^{2-}$  (30ppb).

### 2.3.5 Withstanding pressure of the developed device

The withstanding pressure of the developed device was determined. When the flow restrictor was  $56 \text{ kg/cm}^2$ , the amount of water that leaked on both sides of

the CC and the AC was 0.5% less than that pumped from Inlet2 to Outlet2 without breaking the membrane.

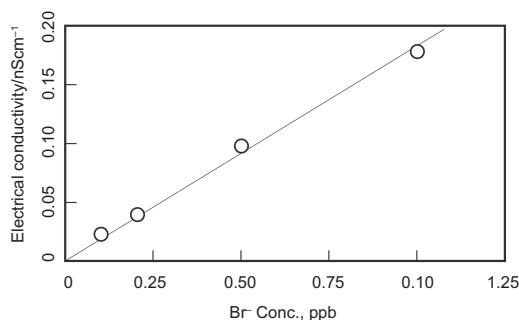


Figure 2.10: Calibration curve of  $\text{Br}^-$ . Sample:  $\text{Br}^-$  (0-1ppb); injection volume ( $20 \mu\text{L}$ ).

### 2.3.6 Detection limit

To confirm that IC equipped with the developed device and a suppressor (Chapter1, iSA8010 [9]) has superior operation properties, Chromatogram of various anions measured by the IC when a pure sodium hydroxide solution of about  $1700 \mu\text{S}/\text{cm}$  produced in-line by the developed device as an eluent is used is shown in Fig. 2.9. As shown in Fig. 2.9, we observe that the reproducibility (coefficient of variation (CV,  $n = 10$ ) of the retention times for standard inorganic anions are below 0.67%, the reproducibility (CV,  $n = 10$ ) of the peak height for fluoride (5ppb), chloride (10ppb), nitrite (15ppb), bromide (10ppb), nitrate (30ppb), sulfate (40ppb) and phosphate (30 ppb) are 1.54, 2.16, 0.39, 1.32, 0.39, 4.59 and 2.07%, respectively, and the detection limits of fluoride, chloride, nitrite, bromide, nitrate, sulfate and phosphate are 0.18, 0.37, 0.9, 2, 1.34, 2.35 and 18ppb, respectively.

Calibration curve of  $\text{Br}^-$  is shown in Fig. 2.10. We observe high linearity between the concentration and the electrical conductivity of bromide. The result corresponds to a linear relationship ( $r = 0.996$ ) with a slope of  $0.174 \mu\text{Scm}^{-1}/\text{ppb}$ . Since the electrical conductivity of the effluent from the separation column is as low as that of ultra-pure water by using IC equipped with the developed device and the suppressor, high-sensitivity detection at the sub-ppb order can be performed. As shown in Fig. 2.11, the anions in tap water are  $\text{F}^-$  (64ppb),  $\text{Cl}^-$  (19.7ppm),  $\text{NO}_3^-$  (9.4ppm),  $\text{CO}_3^{2-}$  (unknown) and  $\text{SO}_4^{2-}$  (19.5ppm).

## 2.4 Conclusions

All the experimental results presented herein are consistent with the described mechanisms. The developed device's container has three compartments (AC, PC,

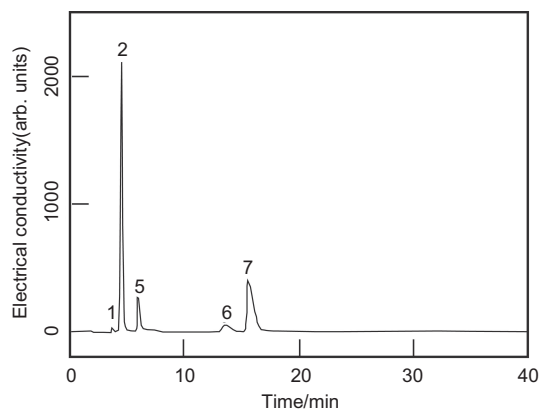


Figure 2.11: Chromatogram of anions in tap water. Sample, tap water, 1,  $F^-$  (64ppb), 2,  $Cl^-$  (19.7ppm), 5,  $NO_3^-$  (9.4ppm), 6,  $CO_3^{2-}$  (unknown), 7,  $SO_4^{2-}$  (19.5ppm).

and CC) separated by two CE membranes and the PC is equipped with two boundaries B1 and B2. Therefore, the NaOH solution generation position of the developed device is separated from the water electrolysis position; thus, the device can tolerate high pressures and produce a high-purity NaOH solution that does not contain gases and impurity anions. Furthermore, the NaOH solution concentration can be controlled precisely and simply by variation in applied current passing through the electrodes. In addition, because the electrical conductivity of NaOH solution generated by this device and a suppressor is as low as that of ultra-pure water, the detection sensitivity of IC is improved, and so the detection limit of anions on the sub-ppb order can be achieved.

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## Chapter 3

# Suppressor for the Ion Chromatography of Cation Analysis

### 3.1 Introduction

In 1975, Small et al. first introduced ion chromatography (IC). They employed a low-capacity anion-exchange (AE) column for the separation of sample anions, in conjunction with a second high-capacity cation-exchange (CE) column and an electrical conductivity detector, which enabled continuous monitoring of the anions. The second column (later termed a suppressor) served to reduce the electrical conductivity of the eluent and increase the electrical conductivity of the cations. This was achieved by exchanging hydroxide ions from the AE suppressor for co-anions (e.g.,  $\text{Cl}^-$ ) in the eluent prior to the measurement of electrical conductivity. The results illustrated that the effluent from the first column was converted to low electrical conductivity (e.g., pure water), and the electrical conductivity of the sample cation was increased as a result of replacing the eluent co-anion by the more electrically conductive hydroxide ion [1].

For the analysis of cations, powerful atomic spectrometry alternatives to IC exist (e.g., ICP-AES/MS), so that the value of cation chromatography is considerably less than that of anion chromatography. However, cation chromatography has achieved a certain importance in the analysis of alkali and alkaline-earth metals and the determination of ammonia nitrogen (e.g., in the analysis of drinking water). In the speciation of ionic compounds, IC in combination with element-specific detectors is indispensable [2–5]. The suppressor technique has grown in use at a phenomenal rate. The following suppressors have been introduced: columns [1], micro-membranes [6–8], and electrolytically regenerated packed-bed suppressors [9–13]. These suppressors are important in that they determine the detection limit in IC. A continuously electrolytically regenerated packed-bed suppressor (known as Atlas) was made available by Dionex in 2001, operates at high eluent concentrations, and has a very low dead volume [12]. Other devices termed electrically regenerated ion-suppression (ERIS) [9, 10] cells and the DS-Plus sup-

pressor [13] have been introduced by Alltech. These devices generate hydroxide and hydrogen ions ( $\text{OH}^-$  and  $\text{H}^+$ ) by the electrolysis of water at the electrodes, and the generated  $\text{OH}^-$  ions act as regeneration ions for neutralizing  $\text{H}^+$  ions in an acidic eluent and converting the eluent into a low-conductivity solution. Both Atlas and ERIS have a recycle mode and an external mode. The suppression capacity, which is the total amount of cations removed from the basic eluent per minute (1 mL/min), is higher in the external mode. However, because the external mode needs two pumps, as external deionized water is used instead of waste fluid from the detector for high-sensitivity detection, the recycle mode, which uses waste fluid from the detector via only one pump, is commonly adopted.

This study aims to develop a new recycle mode suppressor [14, 15], which has high suppression capacity. The device is shown schematically in Fig. 3.1. The container of the device has three compartments filled with ion-exchange resins that are isolated from each other by an AE and a CE exchange membrane, and electrodes are installed at both ends of the container. Each of the compartments is packed with either AE or CE resin. A boundary (B), which is composed of an AE and a CE layer, is present between the electrodes. Anions in the effluent from the separation column are removed by electrical regeneration, which is based on an electrokinetic phenomenon on the surfaces of both the ion exchange resins and the membranes. When a constant current is applied between the electrodes, B serves as a place for the generation of  $\text{H}^+$  ( $\text{D}_\text{H}$ ) and  $\text{OH}^-$  ( $\text{D}_\text{OH}$ ) by the dissociation of water present at B without the electrolysis of water at the electrodes. Therefore, we anticipate that the position where anions are removed is separate from the position where water is electrolyzed; subsequently, a solution containing no gases or anions will be eluted and thus the electrical conductivity of the effluent will reach a level that is similar to that of ultrapure water. This paper describes the introduction of the device that has been developed with B between the electrodes.

## 3.2 Experimental

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

As shown in Fig. 3.1, the developed device consists of a polyetheretherketone container (PEEK, 3 mm i.d., 46 mm length), which is separated by an AE and a CE membrane into the following three compartments. The cathode compartment (CC) (17 mm length), which is packed with CE resin (Amberlite IR120B, 0.6–0.8 mm, 2.0 meq/mL, Dow Chemical), the regeneration compartment (RC) (12 mm length), which is packed with AE resin (Dowex 1X8, 200–400 mesh, 1.4 meq/mL, Dow Chemical), the anode compartment (AC) (17 mm length), which is packed with AE resin (Amberlite IRA402BL, 0.5–0.65 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 Inlet1, Inlet2, and Inlet3 were connected to Pump1 (tubing pump, 1 mL/min of the flow rate is controlled by a homemade flow control driver), Pump2 (1 mL/min, DP-8020, Tosoh, Tokyo, Japan),

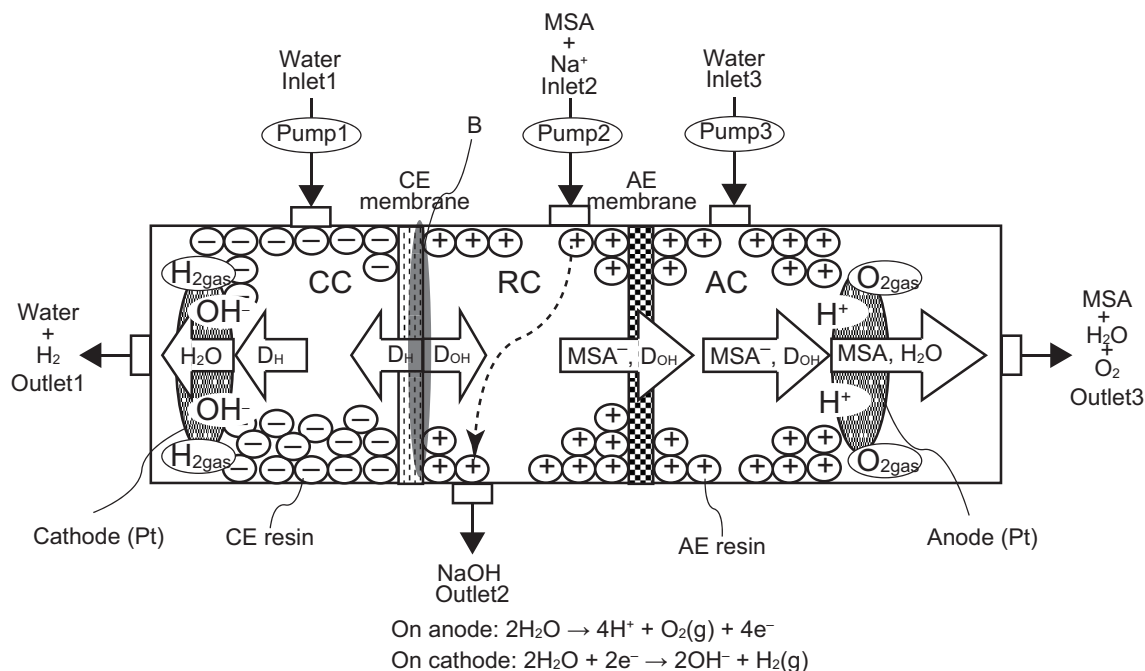


Figure 3.1: Schematic of the developed device to suppress the electrical conductivity of acidic eluent. Reaction at B:  $\text{H}_2\text{O} \longrightarrow \text{H}^+(\text{D}_\text{H}) + \text{OH}^-(\text{D}_\text{OH})$ .

and Pump3 (tubing pump, 1 mL/min of the flow rate was controlled by a home-made flow control driver), respectively. Deionized water (containing trace cations and anions) was pumped into Inlet1 and Inlet3. Electrolyte solution was pumped into Inlet2. The anions contained in the solution were removed. A diagram of the comparing devices (CD) prepared to confirm the proposed mechanisms of the developed device is shown in Figs. 3.2. the CD consists of only an anion exchanger between the electrodes.

### 3.2.2 Acidic and basic solution systems

The acidic and the basic solution system used in this work is shown in Fig. 3.3 and .4, respectively. These systems are assembled using a pump (pump2 shown in Fig. 3.1 and .2), a suppressor for cation analysis (the developed device), an suppressor for anion analysis (iSA8010 [14, 16], Nichiri, Chiba, Japan) and an electrical conductivity detector (ECD, CM432, Nichiri).

### 3.2.3 Ion chromatograph

An ion chromatograph (ICA2000, TOA DKK, Tokyo, Japan) was equipped with a developed device as a suppressor and a cation separation column (TSKgel superIC-CR, 150×4.6 mm i.d., 37 μm, Tosoh). A 2 mM methane sulfonate solution (MSA, about 500 μS/cm) was used as an eluent.



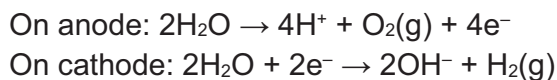
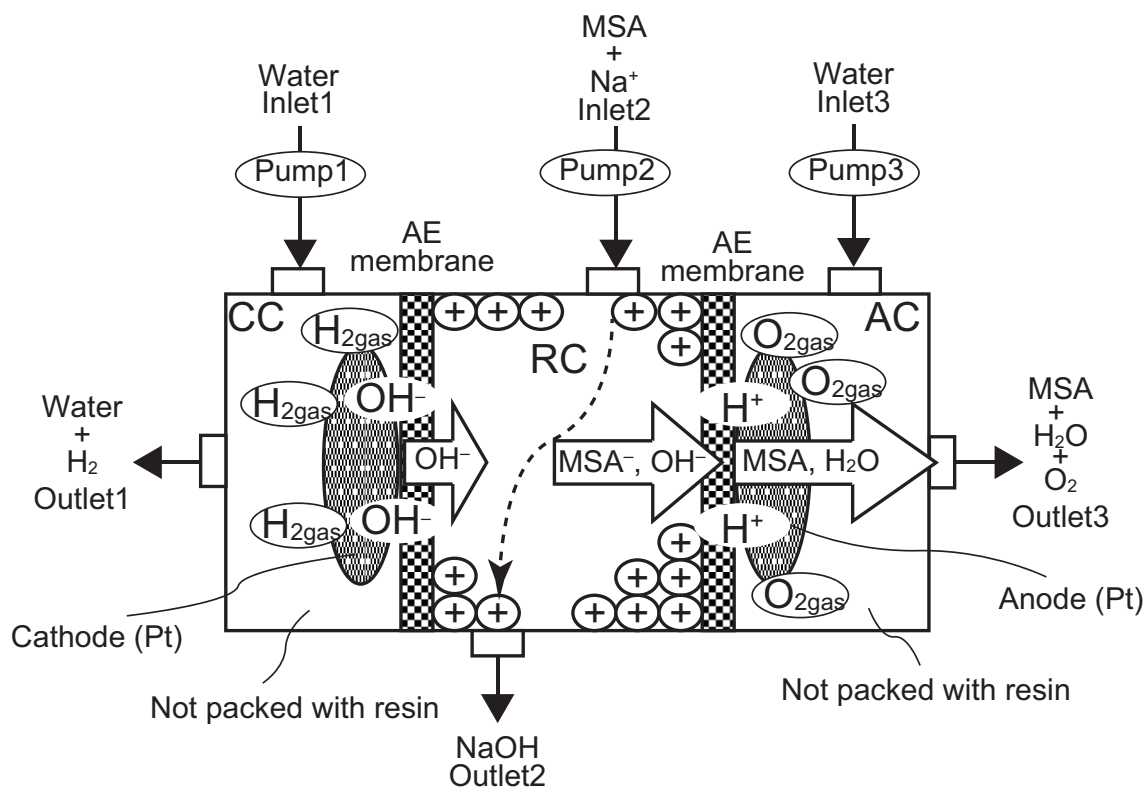


Figure 3.2: Schematic of the CD.

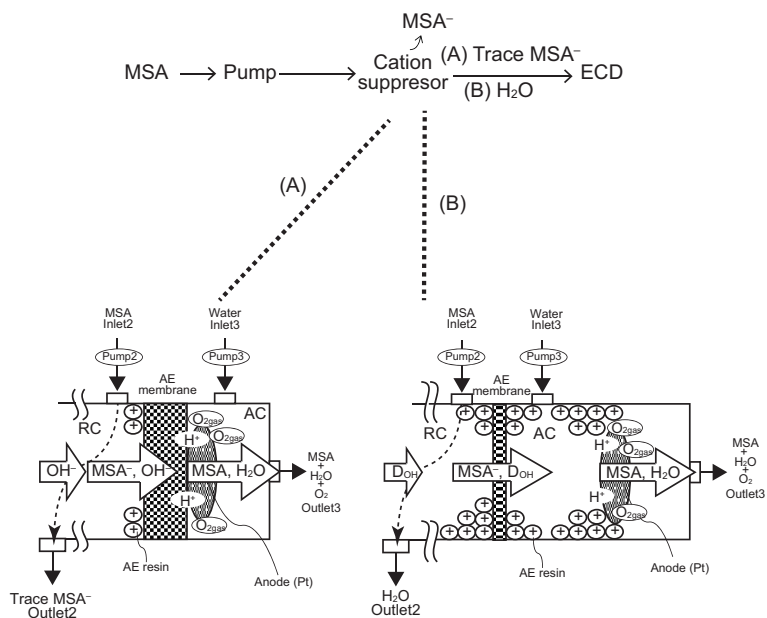


Figure 3.3: Acidic solution system used in this study. (A) the CD, (B) the developed device.

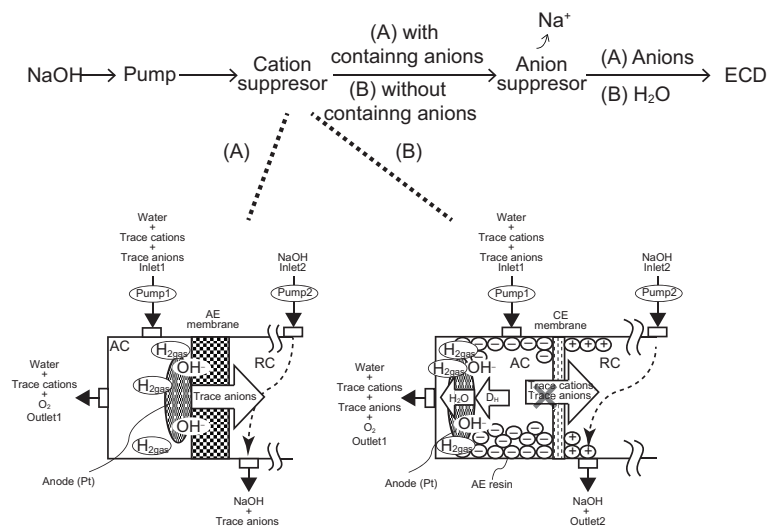


Figure 3.4: Basic solution system used in this study. (A) the CD, (B) the developed device.

## 3.3 Results and Discussion

### 3.3.1 Generation position of $D_H$ and $D_{OH}$

We anticipate that  $D_H$   $D_{OH}$  are generated by the dissociation of water existing at B. The generation positions of  $D_H$ , and  $D_{OH}$  were determined. If the water is not pumped into the RC of the developed device, the water in the RC is consumed by generation of  $D_H$ , and  $D_{OH}$ . Thus, the electrical current through the electrodes will be decreased without the replenishment of  $D_H$ , and  $D_{OH}$ . Variation of the electrical current through the electrodes when the pure water is not pumping into the RC under a constant voltage output 30 V is shown in Fig. 3.5. We observe that current is decreased when the water is not pumped into the RC. The result illustrates that the generation of  $D_H$ , and  $D_{OH}$  is decreased by consumption of water in the RC, and so  $D_H$ , and  $D_{OH}$  are generated by the dissociation of water existing at B.

### 3.3.2 Suppression capacity

The suppression capacity of the developed device was determined. The measurement was used a 20 mM MSA solution (about  $4876 \mu\text{S}/\text{cm}$ ) and carried out using the system as shown in Fig. 3.3. The electrical conductivity of the effluent from the developed device when the electrical current is changed from 0 to 40 mA is shown in Fig. 3.6. We observe that the electrical conductivity is decreased linearly with increasing the applied electric current from 0 to 15 mA, and is  $445 \mu\text{S}/\text{cm}$  when the applied electrical current is 40 mA. The result illustrates that the suppression capacity of the developed device is about  $10 \mu\text{eq}/\text{min}$  (1 mL/min). Since the concentration of MSA solution used as an eluent of the TSKgel superIC-CR is about 2 mM, the developed device has satisfactory suppression capacity in the analysis condition.

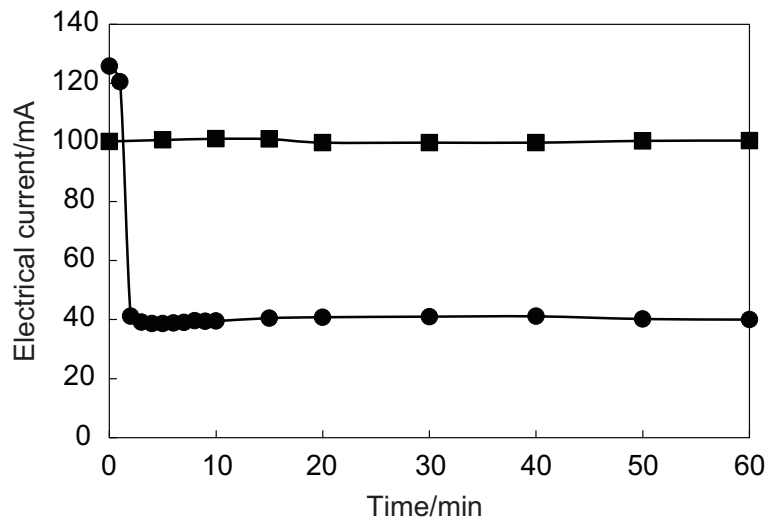


Figure 3.5: Electrical current variation passing through between the electrodes with or without pumping water to the RC of the developed device under a constant voltage output 30 V. without pumping water to the RC, with pumping water to the RC, the AC and the CC.

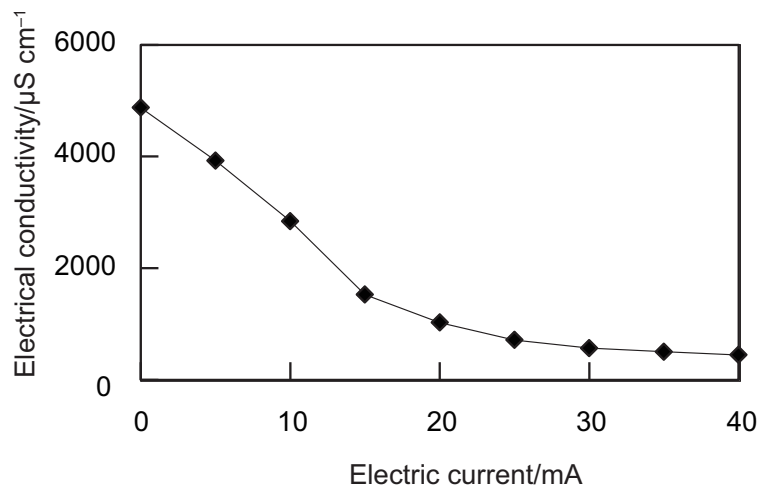


Figure 3.6: Suppression capacity of the developed device.

### 3.3.3 Effect of H<sub>2</sub>O pumped into the AC packed with the AE resin on anion removal

The effect the H<sub>2</sub>O pumped into the AC packed with the AE resin on removing anion was determined. The measurement was used a 6 mM MSA solution (about 1500  $\mu\text{S}/\text{cm}$ ) and carried out using the system as shown in Fig. 3.3. The electrical conductivities of the effluent from the developed device and the CD under a constant electric current of 10 mA were measured. We found that the electrical conductivities of the developed device and the CD were 214 and 950  $\mu\text{S}/\text{cm}$ , respectively, and so electrical conductivity of the developed device was 736  $\mu\text{S}/\text{cm}$  lower than that of the CD. The result illustrate that the amount of cation removed by the developed device is larger than that by the CD. For the CD, although a stream of water was supplied in the AC, because a larger amount of O<sub>2</sub> gas on the cathode was generated, the stream of water could not be supplied to a point of contact between the anode and the AE membrane. Therefore, the amount of MSA<sup>-</sup> on the anode would markedly increase, and so the MSA<sup>-</sup> will move to the RC with the concentration diffusion. For the developed device, because a stream of water was supplied in the AC packed with the AE resin between the AE membrane and the anode, the amount of MSA<sup>-</sup> on the anode will decrease, and so the MSA<sup>-</sup> will not move to the RC with the concentration diffusion. Therefore, the effluent electrical conductivity of the developed device is lower than that of the CD

### 3.3.4 Function of the CE resin and the membrane in the CC

Function of the CE resin and the membrane in the CC was determined under the following assumptions. If trace anions contained in water pumped into the CC are migrated from the CC to the RC by the electrokinetic phenomenon of electrophoresis and the electro-osmotic flow, the anions is eluted from the RC by pumping a 10 mM NaOH (ca. 2000  $\mu\text{S}/\text{cm}$ ) solution to the RC. Because the anions are not removed by the anion suppressor, the anions will be measured by the ECD. The measurement was carried out using the basic system as shown in Fig. 3.4. The electrical conductivities of the effluent from the anion suppressor when the developed device and the CD were used under a constant electrical current of 30 mA were measured. We found that the electrical conductivity of the developed device was 0.12  $\mu\text{S}/\text{cm}$  lower than that of the CD. The result illustrates that the anions are not migrated from the CC to the RC when the developed device is used, and are migrated from the CC to the RC when the CD is used. The result means that the anions migration from the CC to the RC will be prevented by an electrostatic barrier effect for anions of the CE resin and the membrane in the CC.

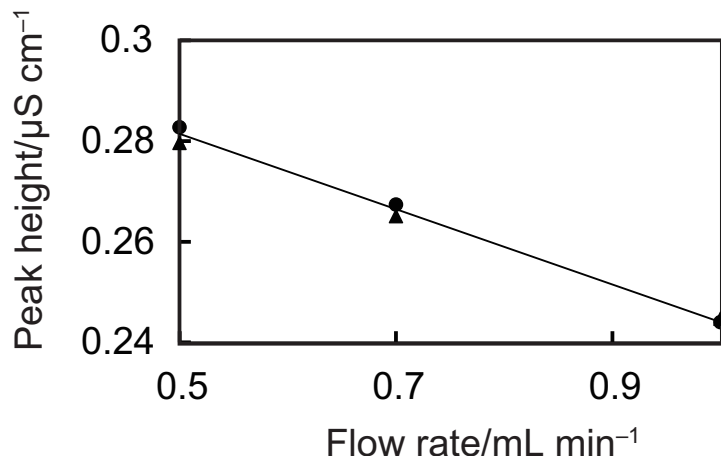


Figure 3.7: Effect of the AE resin in the RC and the CE membrane on preventing cation migration from the RC to the CC. Key:  $\bullet$ , the developed device;  $\blacktriangle$ , the device CD. Sample, 50ppb  $\text{Li}^+$ ; injection volume, 20  $\mu\text{L}$ .

### 3.3.5 Effect of the AE resin in the RC and the CE membranes on preventing cation migration from the RC to the 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 is caused by electrophoresis and the electro-osmotic flow, the amount of cations migrated from the RC to the CC will be increased by decreasing the flow rate of acidic eluent flow in the RC. Variation of  $\text{Li}^+$  concentration eluted from the developed device and the CD when the flow rate of the acidic eluent in the RC is increased from 0.5 to 1 mL/min is shown in Fig. 3.7. We observe that the behaviors of both the developed device and the CD are similar. Because cation migration from the RC to the CC does not occur in the CD, the result illustrates that cation migration from the RC to the CC does not occur in the developed device. We consider that the cations in the RC of the developed device are unable to reach the CE membrane owing to the electro-osmotic flow caused by  $\text{OH}^-$  migration on the AE resin, and so the cations pumped into the RC will be eluted from the RC without absorbing on the AE resin in the RC.

## 3.4 Conclusions

All experimental results described in this paper were consistent with the mechanism described in the Introduction. The developed device's container has three compartments (AC, RC and CC) separated by an AE and a CE membrane. The RC is equipped with one boundary of B. Because the anion removal position is separated from the water electrolysis position, a solution containing no gases and impurity anions can be subsequently eluted from the RC. In addition, the device

has a very low dead volume and high capacity for removal of anions from separation column effluent. Therefore, the device can decrease anions amount of the effluent to a level similar to that of ultrapure water under the recycle mode condition.

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# Chapter 4

## Acid Solution Generator for Ion Chromatography of Cation Analysis

### 4.1 Introduction

Acid solutions have been used widely in the analytical techniques employed by scientists and engineers. Solutions have been used as carriers, eluents, and diluents for techniques, such as HPLC, LC, and titration. In all applications, the acid solutions have been prepared and replenished by the user. This paper specifically addresses the production of methanesulfonate (MSA) and HCl solutions. Conventional methods of preparation of an acid solution involves dilution of concentrated acid; the resulting solutions contain varying amounts of dissolved cations, such as  $\text{Na}^+$ ,  $\text{NH}_4^+$ , and  $\text{K}^+$ . Acid purification involves removing these cations, which is very difficult, time consuming, and often tedious [1]. Therefore, automated methods for acid preparation are desirable. Dasgupta et al have pioneered the application of electrolytic methods to the generation of eluents for ion chromatography (IC) and demonstrated electrical control of concentration [2,3]. Small et al have introduced a new method called ion reflux: eluent generation and suppression have been integrated into an automated form of IC that has the potential to run continuously [4–6]. Dionex has introduced the EG40 eluent generator [6,7], which uses one of two cartridges to produce either a KOH solution (for anion analysis) with a cation exchanger or a methane sulfonic acid (for cation analysis) with an anion exchanger. The concentration of the eluent is controlled by the amount of current that is applied to the ion exchange unit. This device generates MSA solutions by the reaction of  $\text{MSA}^-$  (arriving at the anode) with  $\text{H}^+$  (generated by electrolysis of water on the anode).  $\text{O}_2$  gas is a byproduct of the electrolysis of water. The chemical durability of commercially available anion exchangers is known to be lower than that of cation exchangers.

We propose that a commercially available, chemically tolerant, fluorochemical cation exchange membrane (FCEM) can be inserted between the electrode (anode or cathode) and the anion-exchange(AE) resin to prevent electrolysis of the resin.



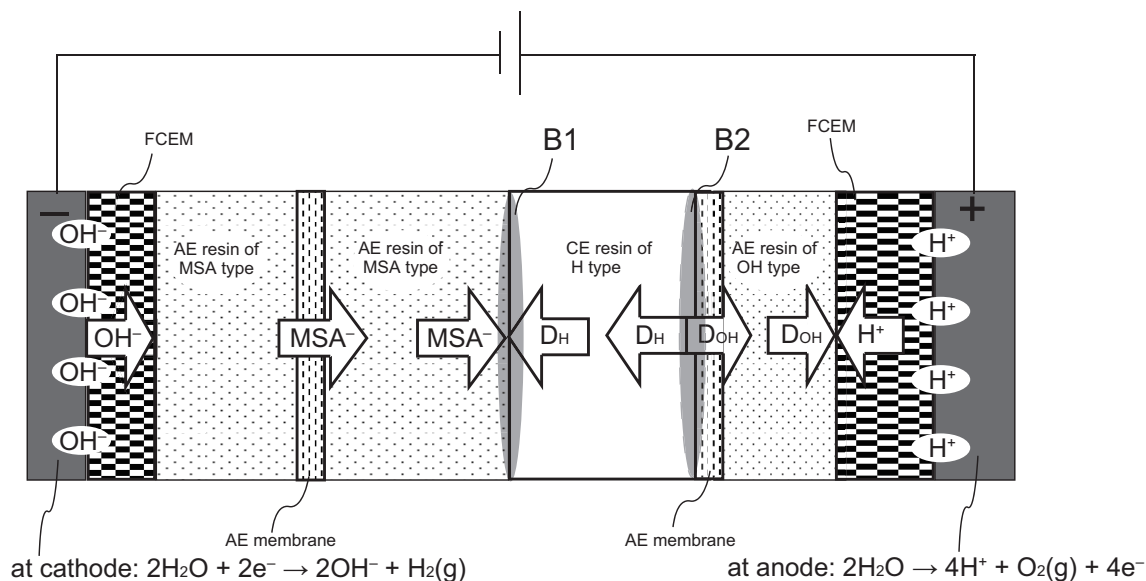


Figure 4.1: Schematic of the device concept. The reaction at B1 is  $\text{H}^+ + \text{MSA}^- \rightarrow \text{HMSA}$ ; the reaction at B2 is  $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ .

The purpose of this study is to develop a new device that produces a continuous stream of a high-purity acid solution [8]. This device must tolerate high pressures, resist degradation from electrolysis on the electrodes, and remove gases ( $\text{H}_2$  or  $\text{O}_2$ ) and cationic impurities from the acid. Our hypothetical device is shown schematically in Fig. 4.1. The device comprises three compartments that are isolated from each other by two AE membranes; electrodes are placed at the far ends of the outside compartments. The three compartments are filled with ion-exchange resins, and the FCEM is installed between each electrode and its adjacent AE resin. A center compartment contains both AE and CE layers packed with AE and CE resins, respectively. Two boundaries are present: B1 separates the MSA anion exchanger from the H cation exchanger and B2 separates the H cation exchanger from the OH anion exchanger. When a constant electrical current is passed between the electrodes, they serve as reaction sites:  $\text{H}^+$  reacts with  $\text{MSA}^-$  at B1 and  $\text{H}^+$  ( $\text{D}_\text{H}$ ) and  $\text{OH}^-$  ( $\text{D}_\text{OH}$ ) are generated by the dissociation of water at B2. Consequently, the acid solution is generated at a separate position from where the water is electrolyzed. These specifications enable the two-boundary device to tolerate high pressures, resist degradation from electrolysis on the electrodes, and produce a high-purity MSA solution that is free from gases and cationic impurities. This paper introduces a device developed for in-line acid generation and examines the mechanism of its operation. A HCl solution is generated by an applied electrical current (0–20 mA) and the resulting concentration varies from 0.01 to 12 mM.

## 4.2 Materials and Methods

### 4.2.1 Architecture of the two-boundary device and the comparison device

The two-boundary device architecture is shown schematically in Fig. 4.1. The device comprises three compartments isolated from each other by two AE membranes (12 mm, AHA, Astom, Tokyo). An electrode is placed at the far ends of the two outside compartments. The cathode compartment (CC, 15 mm in length) is packed with AE resin (Amberlite IRA402BL, 0.6–0.8 mm,  $\geq 1.25$  meq/mL, Organo, Tokyo, Japan) and FCEM1 (CMF, physically modified to increase water permeability, 12 mm, Asahi Glass, Tokyo) is inserted between the cathode and the AE resin. The preparation compartment (PC, 15 mm in length) consists of both cation- and anion-exchanger phases. The CE phase comprises CE resin (Dowex 5WX8, 200–400 mesh, 1.7 meq/mL, Acros Organics, New Jersey, USA); the AE phase comprises AE resin (Dowex 1X8, 200–400 mesh, 1.2 meq/mL). The anode compartment (AC, 15 mm in length) is filled with AE resin (Amberlite IRA402BLB), and FCEM2 (CMF) is installed between the cathode and the AE resin. Inlet1, Inlet2, and Inlet3 are connected to Pump1 (tubing pump, with a 1 mL/min flow rate controlled by a home-made flow control driver), Pump2 (1.3 mL/min, DP-8020, Tosoh, Tokyo, Japan), and Pump3 (tubing pump, with a 1 mL/min flow rate controlled by a home-made flow control driver), respectively. A 100 mM MSA solution is pumped into Inlet1, pure water is pumped into Inlet2 and Inlet3, and the purified MSA solution is eluted from Outlet2.

A comparison device ( $CD_{\text{boundary0}}$ ) was built to test the proposed mechanisms of the two-boundary device; they are shown schematically in Fig. 4.3. the  $CD_{\text{boundary0}}$  is packed with the AE resin instead of the CE resin, so the boundary between the CE resin and the anion exchanger does not exist. The generated MSA solution elutes from Outlet3.

### 4.2.2 Electrical conductivity measurement of the MSA solution produced by the two-boundary device and the $CD_{\text{boundary0}}$

Outlet2 of the two-boundary device, as well as Outlet3 of the  $CD_{\text{boundary0}}$ , was connected to an electrical conductivity detector (ECD, iCM8401, Nichiri, Japan) to measure the electrical conductivity of the effluent streams.

### 4.2.3 Ion chromatography for the qualitative analysis of cationic impurities in the generated MSA solution

An ion chromatograph (ICA-2000) was equipped with a pump (1 mL/min, ICA-2000), an injector (20  $\mu$ L, ICA-2000), a separation column (IonPac CS14, 40 cm, Dionex, USA), a suppressor (iSC8010 [9], Nichiri), and an electrochemical detector (ECD, ICA-2000). Effluent ( $\sim 10$  mM MSA solution,  $\sim 3861$   $\mu$ S/cm, pH 2.04) from

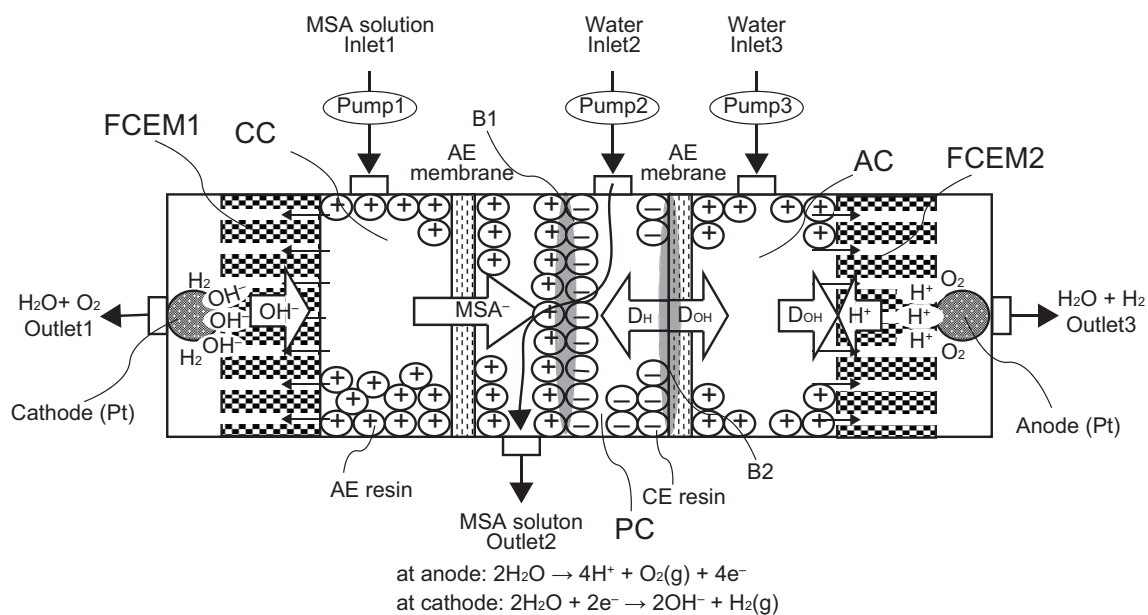


Figure 4.2: Schematic of the two-boundary device Reaction at B1:  $\text{H}^+ + \text{MSA}^- \rightarrow \text{HMSA}$ , reaction at B2:  $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$ .

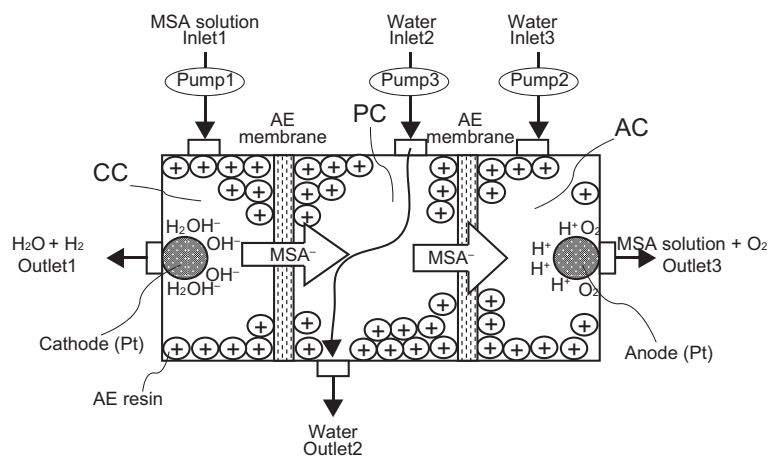
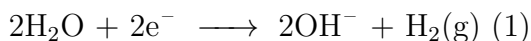


Figure 4.3: Schematic of the  $\text{CD}_{\text{boundary0}}$

Outlet2 of the two-boundary device was fed via a tee into the ICA-2000 pump and used as an eluent for IC. The injected sample was separated using columns,  $\text{MSA}^-$  was removed from the eluent using the suppressor, and the suppressor effluent was characterized by the ECD.

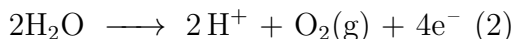
#### 4.2.4 Mechanisms

Ion-exchange resins and membranes have mobile counter ions and are good electronic conductors [10, 11]. We consider an ion exchanger between two metal electrodes in a chamber pumped with water. When a DC potential is applied across the electrodes, the electrical field drives the positive counter ions to move toward the cathode and the negative counter ions to move toward the anode. The cathodic reduction of water produces  $\text{OH}^-$  and  $\text{H}_2$  gas:



$\text{H}_2$  gas is eluted out with the MSA solution passing from Inlet1 to Outlet1 because the CC is separated from the PC by the CE membrane. Trace amounts of  $\text{NH}_4^+$  in the MSA solution are also eluted out with the stream. FCEM1 is installed between the cathode and the AE resin of the CC. The  $\text{OH}^-$  generated on the cathode migrates sequentially through FCEM1 to the AE resin in the CC, and then into the AE resin in the PC. As a single anion migrates, it displaces other anions ( $\text{OH}^-$  and  $\text{MSA}^-$ ), propagating a net motion toward the anode.

The PC has two boundaries (B1 and B2). B1 is between the CE resin and the AE resin; B2 is between the AE membrane and the CE resin. The CE resin is a negatively charged stationary phase; anions, such as  $\text{OH}^-$ ,  $\text{Cl}^-$ , and  $\text{MSA}^-$ , collect and concentrate at B1.  $\text{D}_\text{H}$  and  $\text{D}_\text{OH}$  are generated by the dissociation of water at B2.  $\text{D}_\text{H}$  and  $\text{D}_\text{OH}$  migrate toward B1 and the anode, respectively. If water is depleted in the CC and/or the PC, the electrical current will not pass between the electrodes because there is no means for replenishing the population of  $\text{OH}^-$  anions,  $\text{D}_\text{H}$ , or  $\text{D}_\text{OH}$ . Consequently, water has to be pumped into the CC and the PC to maintain a constant electrical current between the electrodes. The  $\text{MSA}^-$  that is concentrated at B1 reacts with  $\text{D}_\text{H}$  because the PC is separated from the AC and the CC by two AE membranes; the reacted MSA solution is eluted out with water passing from Inlet2 to Outlet2 across B1. The anodic oxidation of water produces  $\text{O}_2$  gas and  $\text{H}^+$ :



FCEM2 is placed between the anode and the AE resin of the AC. The  $\text{H}^+$  generated by the electrolysis of water on the anode migrates through FCEM2 to the AE resin of the AC. The molar quantity of  $\text{H}^+$  is identical to that of  $\text{D}_\text{OH}$  arriving at FCEM2.

$\text{O}_2$  gas is eluted out with pure water passing from Inlet3 to Outlet3 because the AC is separated from the PC by the AE membrane. Cationic impurities and anions in the water are also eluted out with the stream.

In the two-boundary architecture, the MSA solution is generated at one spatial boundary that is separate from where the water is electrolyzed. As a result, high-purity MSA solutions can be prepared in-line and are free from gases and cationic impurities.

## 4.3 Results and Discussion

### 4.3.1 Location of generated $H^+$ , $OH^-$ , $D_H$ , and $D_{OH}$ and the water needed to maintain a constant electrical current between the electrodes

We determined the locations where  $H^+$ ,  $OH^-$ ,  $D_H$ , and  $D_{OH}$  were generated.  $H^+$  and  $OH^-$  were generated by the electrolysis of water on the electrodes;  $D_H$  and  $D_{OH}$  were generated by the dissociation of water at B2. If water is not continuously pumped into the PC of the two-boundary device, it is consumed by the generation of  $D_H$  and  $D_{OH}$ , and the electrical current passing between the electrodes decreases. If water is not continuously pumped into the AC or the CC, it is consumed by electrolysis. Thus, the electrical current between the electrodes will decrease if  $H^+$  and  $OH^-$  are not replenished. The variation in the electrical current at a constant potential of 30 V is shown in Fig. 4.4 when the water flow is withheld from each of the three compartments in turn. The electrical current decreases when the flow of water is withheld from the PC or the CC; it increases when water is withheld from the AC Fig. 4.4. The experimental result exhibiting that the electrical current decreases when water is withheld from the CC and the PC illustrates that the generation of  $OH^-$ ,  $D_H$ , and  $D_{OH}$  decreases due to consumption of the water in these compartments. The cause of the electrical current increase when water is withheld from the PC and the AC is unknown. The experimental result exhibiting that the electrical current does not decrease when water is withheld from the AC indicates that trace amounts of water are supplied to the cathode by electroosmotic flow from B2, and water in the AC is not consumed. These results verify that  $H^+$  and  $OH^-$  are generated by the electrolysis of water on the electrodes, and  $D_H$ , and  $D_{OH}$  are generated by the dissociation of water at B2.

### 4.3.2 Electrical-chemical durability of the two-boundary device resulting from FCEM1 and FCEM2

We determined the extent to which FCEM1 and FCEM2 prevented the electrochemical degradation of the AE resin packed in the AC and the CC. We had hypothesized that the AE resin was degraded by electrolysis on the electrodes. When the AE resin degraded, electrical current could not pass between the electrodes, and the voltage increased at a constant current. Variations in the voltage were measured for a constant current of 40 mA with and without the two membranes; the results are shown in Fig. 4.5. The potential across the electrodes is greater than 90 V when the membranes are absent, and the voltage is constant

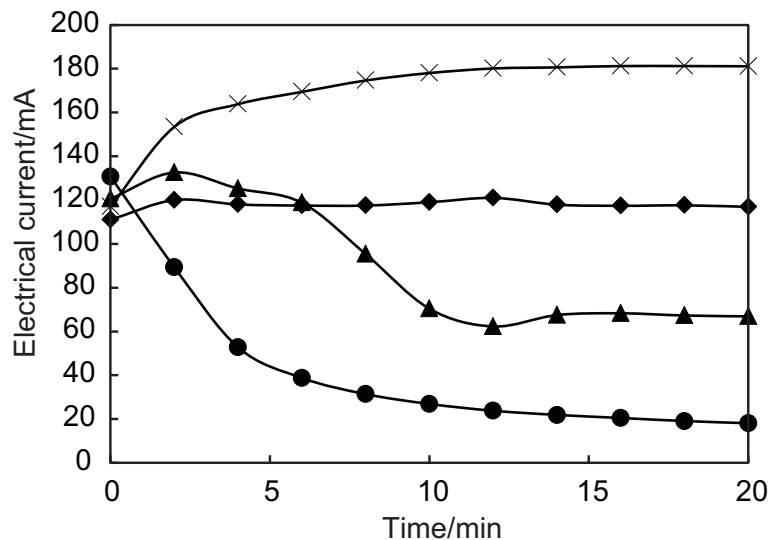


Figure 4.4: Variation in the applied electrical current as a function of time for a constant potential of 30 V in the two-boundary device: ( ◊ ) water is withheld from the PC, ( × ) water is withheld from the AC, ( ● ) water is withheld from the CC, ( ▲ ) water is pumped to all compartments (PC, AC, and CC).

when they are present. This result shows that the electrical-chemical durability of the system increases when FCEM1 and FCEM2 are placed on the electrodes.

### 4.3.3 Spatially separating the generation of the MSA solution from gas evolution

The electrical conductivity of effluent from the two-boundary device was measured to confirm that gases generated in the system were not contained in the MSA solution that was generated. A well-known characteristic of ECDs is that they produce spike-like noise when a gas is present in the analyte solution. The electrical conductivity of the MSA solution ( $\sim 10$  mM,  $\sim 3840$   $\mu\text{S}/\text{cm}$ ) generated by the device is shown in the left panel of Fig. 4.6. For comparison, the electrical conductivity of the MSA solution ( $\sim 10$  mM,  $\sim 3840$   $\mu\text{S}/\text{cm}$ ) produced by the  $\text{CD}_{\text{boundary}0}$  is shown in the right panel of Fig. 4.6. Clearly, spike-like noise is not evident in the effluent of the two-boundary device and is evident in the effluent of the  $\text{CD}_{\text{boundary}0}$ . This proves that the MSA solution produced by the two-boundary device is free from gas. We conclude that the two-boundary device separates the location where MSA solution is generated from the location where water is electrolyzed.

### 4.3.4 Performance of the two-boundary device: purity of the MSA solution

To estimate the performance of the two-boundary device, the concentration of cationic impurities was determined in a sample of the generated MSA solution. Ultra-pure water (without ions) was pumped into the PC of the two-boundary

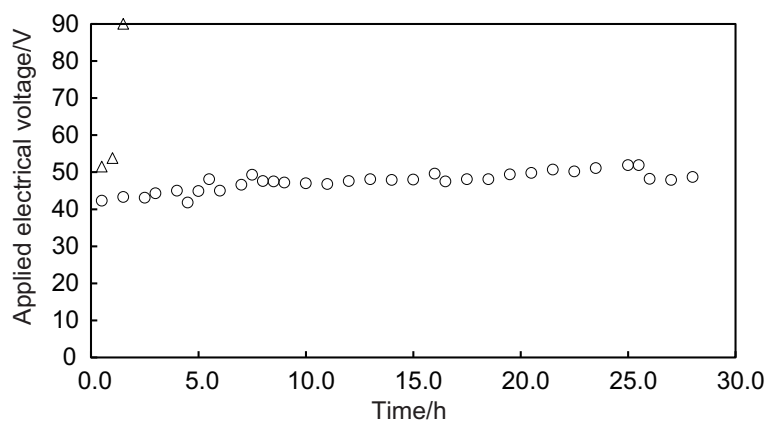


Figure 4.5: Effect of FCEM1 and FCEM2 on the potential across the electrodes as a function of time: (  $\Delta$  ) both membranes are present and (  $\circ$  ) both membranes are absent.

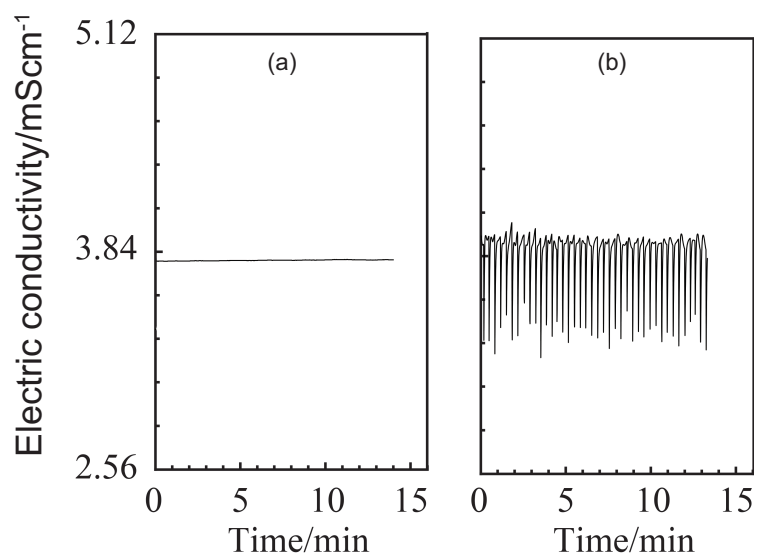


Figure 4.6: Electrical conductivity of the MSA solution generated by the two-boundary device and the  $CD_{\text{boundary}0}$ : (a) the two-boundary device and (b) the  $CD_{\text{boundary}0}$ .

device. A chromatogram of the MSA solution ( $\sim 10$  mM,  $\sim 3861 \mu\text{S}/\text{cm}$ , pH 2.04) generated by the two-boundary device is shown in Fig. 4.7(c). For comparison, an MSA solution was prepared by the conventional method (10 mM MSA prepared from a 1 M MSA stock solution,  $3882 \mu\text{S}/\text{cm}$ , pH 2.05); the chromatogram is shown in Fig. 4.7(b). Cations are not present in the MSA solution generated by the two-boundary device, whereas they are present in the conventionally prepared solution. This indicates that the cations do not migrate from the CC and the AC into the PC of the two-boundary device. If ultra-pure water is pumped into the PC, the two-boundary device can generate a high-purity MSA solution

### 4.3.5 Concentration of the HCl solution generated by the two-boundary device

A HCl solution was generated by pumping 200 mM NaCl solution (instead of 100 mM MSA solution) into the CC of the two-boundary device. The resulting concentration of HCl was determined. The concentration of the HCl solution can be estimated from the electrical conductivity value measured by ECD [12]. The electrical conductivity of the HCl solution is shown as a function of the applied current in Fig. 4.8. The relationship between the concentration of HCl and the applied current is linear ( $r = 0.999$ ) with a slope of  $0.566 \text{ mM}/\text{mA}$ . In a separate experiment, the electrical current applied was fixed at 5 mA, and the electrical conductivity of the purified HCl solution was measured to be  $1186 \mu\text{S}/\text{cm}$ , corresponding to a HCl concentration of 2.84 mM. The electrical current was increased to 10 mA, and the concentration increased to 5.81 mM. This result confirms the linear dependence of the concentration of the HCl solution on the applied electrical current. We have demonstrated the ability to control the concentration of the HCl solution using the applied electrical

### 4.3.6 Pressure resistance of the two-boundary device

The pressure resistance of the two-boundary device was determined. A flow restrictor generated a pressure of  $56 \text{ kg}/\text{cm}^2$ , causing less than 0.5% of the water pumped from Inlet2 to Outlet2 to leak into the CC and the AC. Moreover, the membranes in the system did not break during the pressure test.

### 4.3.7 Detection limit

The performance of IC equipped with the developed device and a suppressor for cation analysis were demonstrated. The detection limits of various cations were determined. As can be seen from the chromatograms of standard inorganic cations shown in Fig. 4.9, the signal intensity of the water dip is lower with the developed device than without those. When those device are used, the reproducibility (CV,  $n = 10$ ) of the peak height for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  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  $\text{Li}^+$  shown in Fig. 4.10, the signal intensity of the cations with those device is about half that without those. However, the



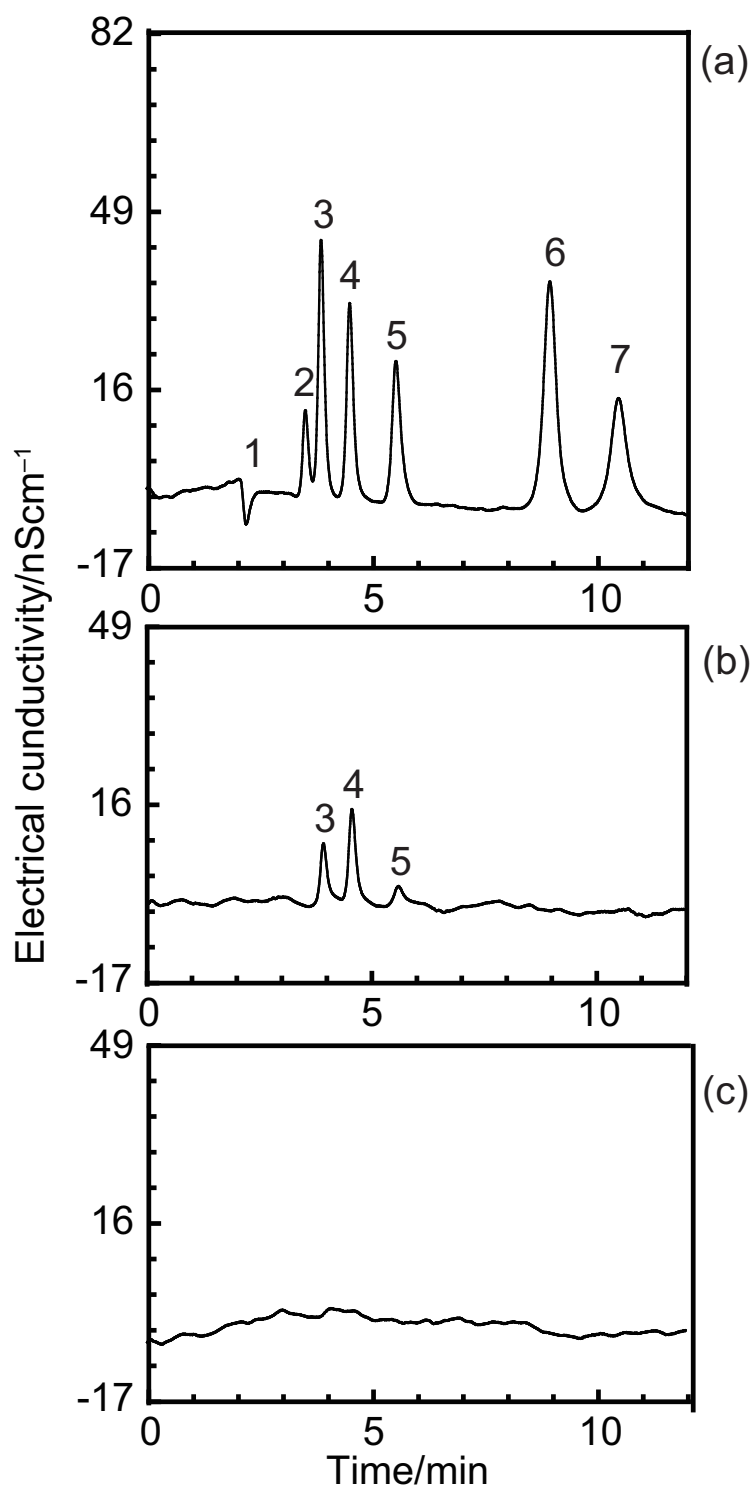


Figure 4.7: Electrical conductivity as a function of time to assay cations: (a) standard inorganic anions (1) water dip, (2)  $\text{Li}^+$  (5ppb), (3)  $\text{Na}^+$  (20ppb), (4)  $\text{NH}_4^+$  (20ppb), (5)  $\text{K}^+$  (50ppb), (6)  $\text{Mg}^{2+}$  (50ppb), and (7)  $\text{Ca}^{2+}$  (50ppb); (b) 10 mM MSA solution prepared from 1 M MSA solution stock (3)  $\text{Na}^+$  (4.8ppb), (4)  $\text{NH}_4^+$  (9.2ppb), and (5)  $\text{K}^+$  (5.6ppb); and (c)  $\sim 10$  mM MSA solution generated by the two-boundary device.

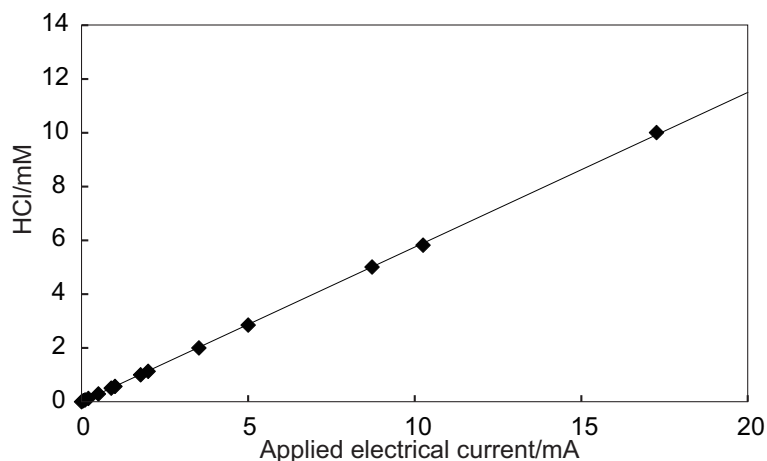


Figure 4.8: Specific concentration of the MSA solution generated by the two-boundary device as a function of the applied electrical current.

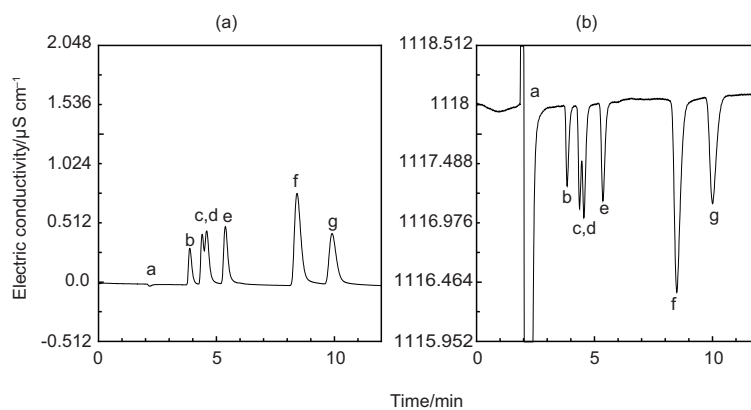


Figure 4.9: Chromatograms of standard inorganic cations. (a) With the developed device, (b) without the developed device. Samples, (1)  $\text{Li}^+$  (50ppb), (2)  $\text{Na}^+$  (200ppb), (3)  $\text{NH}_4^+$  (200ppb), (4)  $\text{K}^+$  (500ppb), (5)  $\text{Mg}^{2+}$  (500ppb), (6)  $\text{Ca}^{2+}$  (500ppb); eluent, 2 mM MSA (0.7 mL/min).

noise intensity with those devices is about 1/50 smaller than that without those devices. The detection limit of  $\text{Li}^+$  with and without those devices is 0.09 and 2ppb, respectively ( $S/N = 3$ ). The correlation coefficient of the calibration curve with and without those devices between 0 and 500 ppb was 0.999 and 0.998, respectively.

## 4.4 Conclusions

All the experimental results presented in this paper were consistent with the described mechanisms. The developed device's container has three compartments (AC, PC and CC) separated by two AE membranes and the PC is equipped with two boundaries of the B1, B2 for separating the MSA solution generation position from the water electrolysis position. In addition, the AC and the CC are equipped

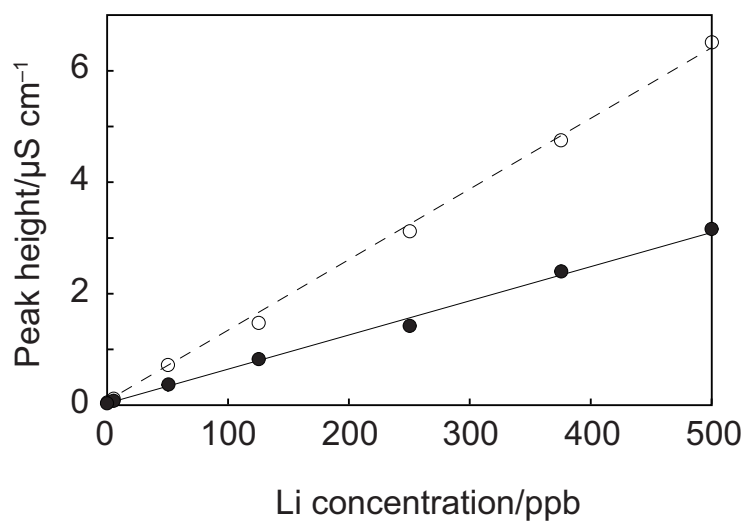


Figure 4.10: Calibration curve of  $\text{Li}^+$ . Key:  $\bullet$ , with the developed device;  $\circ$ , without the developed device. Eluent, 2 mM MSA (0.7 mL/min).

with the FCEM1 and the FCEM2 to preventing the electrolysis of the AE resin on the electrodes, respectively. Therefore, the device can tolerate high pressures, electrolysis on the electrodes, and produce a desired high purity MSA solution without containing the gases and impurity cations. The MSA solution concentration can be precisely and simply controlled by variation of the applied electrical current passing through between the electrodes. In one more, because the electrical conductivity of acid solution generated by this device and a suppressor is as low as that of ultra-pure water, the detection sensitivity of IC is improved, and so the detection limit of cations on the sub-ppb order can be achieved.

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# Chapter 5

## Anion Analysis Using CO<sub>2</sub> Remover

### 5.1 Introduction

In 1975, Small et al. introduced ion chromatography (IC) [1], which is now widely used in engineering, science, as well as other fields. Most ion chromatographs are equipped with a suppressor and an electrical conductivity detector (ECD). Alkaline hydroxide solutions, such as LiOH, NaOH, and KOH, and carbonate buffer solutions have been mainly used as the eluents for IC anion analysis. Although the detection sensitivity is improved using the hydroxide eluents, the preparation and the maintenance of pure hydroxide eluents is very difficult [2]. While an ion chromatograph equipped with an in-line hydroxide generator has been reported [3], the system is very expensive. Because the sensitivity of IC with the carbonate buffer eluents is lower than that with hydroxide eluents, a post-suppression degassing method for the removal of the CO<sub>2</sub> contained in the effluent from the suppressor [4–7] was developed in the 1980s for improving the detection performance. However, because this method uses gas permeable tubing (GPT), such as a silicone rubber [8–11, 13] or poly(tetrafluoroethylene) (PTFE) [4, 6, 7], it has two problems.

First, the peak band of the sample eluted from the separation column is broadened by diffusion through the GPT.

Second, the GPT is constrained by its pressure and chemical resistance. In 2002, Saari-Nordhaus et al. reported a new post-suppression degassing device using Teflon AF tubing, which was developed in the 1990s, for the GPT to overcome these problems, [9–16]. This device consisted of a suppressor and a CO<sub>2</sub> remover. The suppressor removed the cations contained in the effluent, and the HCO<sub>3</sub><sup>-</sup> (CO<sub>3</sub><sup>2-</sup>) in the effluent was converted to CO<sub>2</sub> (H<sub>2</sub>CO<sub>3</sub>) gas. The CO<sub>2</sub> remover consisted of a closed vessel equipped with Teflon AF tubing and a CO<sub>2</sub> adsorbent. The CO<sub>2</sub> gas was selectively removed from the suppressed effluent via the diffusion of CO<sub>2</sub> from the inside of the GPT to the vessel, due to the CO<sub>2</sub> partial pressure difference between the inside of the GPT and the vessel created by adsorption of CO<sub>2</sub> gas in the vessel by the CO<sub>2</sub> adsorbent. Although the properties

of the CO<sub>2</sub> remover, such as the water content of the adsorbent, the temperature, and the quantity of the adsorbent, possibly have an effect on the amount of CO<sub>2</sub> removed, the paper by Saari-Nordhaus et al. does not discuss these concerns in any detail.

This paper describes the introduction of a practicable CO<sub>2</sub> gas removal device existing of a commercially available polypropylene-nonwoven fabrics pack (PNFP) for tea leaves, which is packed with a substantially dry OH<sup>-</sup> type anion-exchange (AE) resin [17]. The purpose of this study is to optimize the operating conditions, including the temperature, quantity of adsorbent, etc., with the aim of selectively removing HCO<sub>3</sub><sup>-</sup> (CO<sub>3</sub><sup>2-</sup>) contained in the effluent and reducing the electrical conductivity of the effluent under non-vacuum conditions.

## 5.2 Materials and Methods

### 5.2.1 Preparation of the OH<sup>-</sup> type anion exchange resin

Amberlite IRA402BL (Cl type, Dow Chemical, 0.50–0.65 mM, 1.25 eq/L) was obtained from Organo Corp. The Cl type IRA402BL was exchanged to an OH-type using aqueous 2–4% NaOH as the regeneration solution. The exchanged resin was washed with pure water produced using an SA-2000E1 ( < 1 μS/cm, EYELA), then was with acetone, and substantially dried using a reduced-pressure drying method.

### 5.2.2 CO<sub>2</sub> adsorbent

A polypropylene-nonwoven fabric pack (PNFP) packed with the substantially dried OH<sup>-</sup> type AE resin was used as the CO<sub>2</sub> adsorbent. The quantity of resin packed in PNFP was 20 g, unless otherwise indicated.

### 5.2.3 CO<sub>2</sub> remover

A diagram of the CO<sub>2</sub> remover is shown in Fig. 5.1. The device consists of a closed vessel (conical flask, 300 mL) equipped with a GPT (AF2400 tubing, I.D: 0.25 mm, O.D: 0.5 mm, length: 4 m, U-VIX Corp., Tokyo, Japan) and the PNFP packed with AE resin. In addition, because the pressure increases as the temperature in the vessel increases, the vessel is equipped with a port and a valve for release of the internal pressure such that atmospheric pressure can be maintained. The temperature in the vessel is controlled using a heater installed outside of the vessel. In the present study, the temperature in vessel was 37 °C unless otherwise indicated. The valve was left open until the temperature of the vessel reached the set temperature and then closed.

### 5.2.4 System for estimation of CO<sub>2</sub> removal

A diagram of the system used to estimate the CO<sub>2</sub> removal is shown in Fig. 5.2. The system consists of a pump (1 mL/min, DP-8020, Tosoh, Tokyo, Japan), a

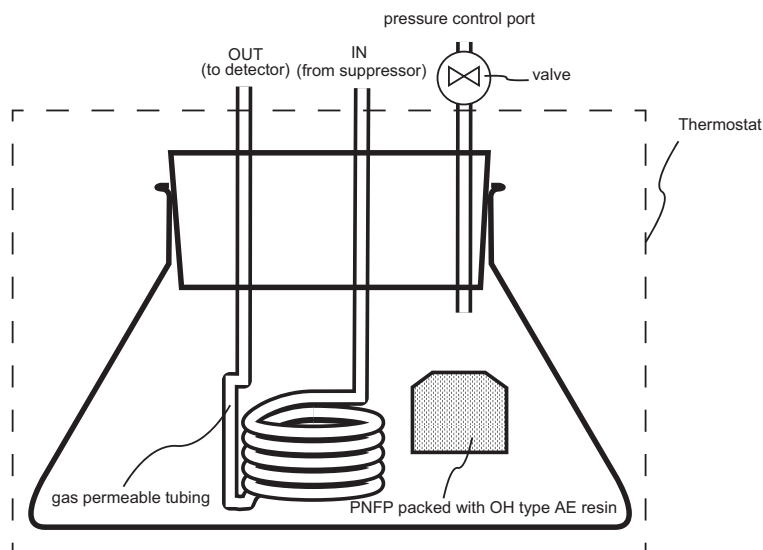


Figure 5.1: Schematic of a CO<sub>2</sub> remover

suppressor (iSA8010 [18,19], Nichiri, Chiba, Japan), a CO<sub>2</sub> remover, and an ECD (ICA-2000, TOA DKK, Tokyo, Japan). Two types of carbonate buffer solutions (1 L) were prepared and pumped into the system: type (A) solution consisted of 12 mM NaHCO<sub>3</sub> + 0.6 mM Na<sub>2</sub>CO<sub>3</sub> (ca. 850 μS/cm, pH 8.9) and could not represent the HCO<sub>3</sub><sup>-</sup> (CO<sub>3</sub><sup>2-</sup>) peak contained in the sample; type (B) solution was comprised of 1.8 mM Na<sub>2</sub>CO<sub>3</sub> + 1.7 mM NaHCO<sub>3</sub> (ca. 435 μS/cm, pH 10), which is commonly used as a carbonate eluent for IC. The Na ions were removed from the pumped carbonate buffers with the aid of the suppressor, and then CO<sub>2</sub> gas was removed from the suppressor effluent with the aid of the CO<sub>2</sub> remover. The electrical conductivity of the CO<sub>2</sub> remover effluent was detected using the ECD.

First, the quantity of OH<sup>-</sup> type AE resin required for 12 h of continuous operation was determined by measuring the electrical conductivity of the effluent from the CO<sub>2</sub> remover containing a PNFP packed with different amounts of OH-type AE resin amounts (1 , 2 , 5 , and 10 g).

Second, the effect of the water content in the OH<sup>-</sup> type AE resin on the adsorption of CO<sub>2</sub> gas in the vessel was investigated by measuring the electrical conductivity of the effluent from the CO<sub>2</sub> remover when different quantities (1, 2, 5, and 10 mL) of pure water were added to 10 g of the OH<sup>-</sup> type AE resin packed in the PNFP.

Third, the effect of the GPT length on the removal of CO<sub>2</sub> from the suppressor effluent pumped into the GPT was investigated by measuring the electrical conductivity of the effluent from the CO<sub>2</sub> remover using GPTs of varying lengths (0, 1, 2, 3, 4, and 5 m).



Figure 5.2: Schematic of the system for estimating CO<sub>2</sub> removal.

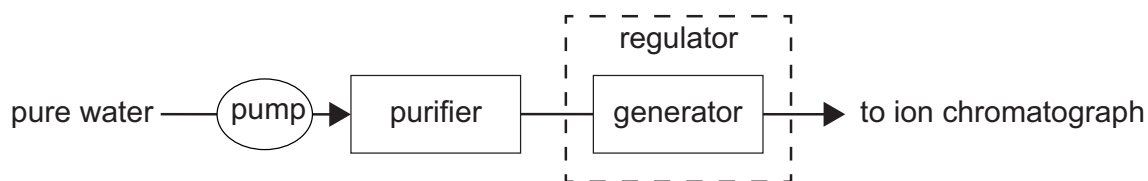


Figure 5.3: Schematic of the system for generating a pure, in-line NaOH solution.

Fourth, the effects of the PNFP and the temperature in the vessel on the removal of CO<sub>2</sub> from the suppressor effluent were investigated by measuring the electrical conductivity of the effluent from the CO<sub>2</sub> remover when the pressure and the temperature in the vessel without the PNFP were 7.9 kPa and 50 °C and with the PNFP were 100 kPa and 50 °C and 100 kPa and 80 °C, respectively.

Finally, the decrease in the electrical conductivity using the CO<sub>2</sub> remover under optimized conditions was calculated by determining the difference in the electrical conductivities with and without the optimized CO<sub>2</sub> remover.

### 5.2.5 System to generate a pure NaOH solution in-line

A diagram of the system for generating pure NaOH solutions in-line is shown in Fig. 5.3. The system consists of a pump (pure water, 1.3 mL/min, CCPM, Tosoh), a purifier (suppressor for cation analysis [18, 20], iSC8010, Nichiri), a generator (Nichiri), and a regulator (Nichiri). Pure water was pumped into the system, and then HCO<sub>3</sub><sup>-</sup> (CO<sub>3</sub><sup>2-</sup>) and CO<sub>2</sub> gas were removed from the pumped pure water with the aid of a purifier. A NaOH solution of a desired concentration was then produced using the generator and the regulator. The generated NaOH solution was subsequently pumped to an ion chromatograph and used as the eluent.

### 5.2.6 Ion chromatograph for evaluation of IC with the aid of the CO<sub>2</sub> remover

A diagram of the ion chromatograph used to evaluate IC performance with the aid of the CO<sub>2</sub> remover is shown in Fig. 5.4. The ion chromatograph (ICA-2000) is equipped with a pump (1 mL/min, ICA-2000), an injector (20 μL, ICA-2000), a separation column (37 cm, PCI-205, TOA DKK), a suppressor (iSA8010, Nichiri), the CO<sub>2</sub> remover, and an ECD (ICA-2000). An NaOH solution (15 mM, ca. 2320 μS/cm, pH 12.1) generated in-line using the system shown in Fig. 5.3 or a type (A) carbonate buffer were used as the eluents. The injected sample was separated using the separation column, Na ions were removed from the eluent with



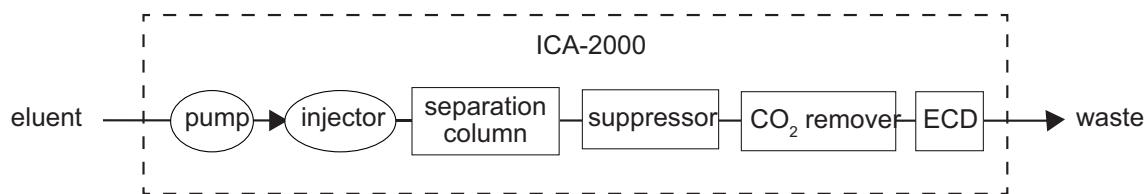


Figure 5.4: Schematic of the ion chromatograph for evaluation of IC with the aid of the CO<sub>2</sub> remover.

aid of the suppressor, CO<sub>2</sub> gas was removed from the suppressor effluent using the CO<sub>2</sub> remover, and then the CO<sub>2</sub> remover effluent was analyzed using the ECD.

## 5.3 Results and Discussion

### 5.3.1 Determination of the required quantity of OH<sup>-</sup> type AE resin for 12 h of continuous operation

As shown in the graph in Fig. 5.5, the electrical conductivity of the effluent from the CO<sub>2</sub> remover varies between 0.85 and 1.28 μS/cm at the starting time and decreases to 0 μS/cm, after 10 min independent of the quantity of the OH<sup>-</sup> type AE resin in the PNFP. From 10 to 50 min, the electrical conductivity of the effluent from the CO<sub>2</sub> remover remains stable for all the prepared quantities of the OH<sup>-</sup> type AE resin used. At approximately 50 min the electrical conductivity starts to increase when PNFP is packed with 1 g of the OH<sup>-</sup> type AE resin. The quantity of CO<sub>2</sub> adsorbed by 1 g of OH<sup>-</sup> type AE resin in the PNFP after 60 min was approximately 759 μmol as estimated using the following equations:

Quantity of HCO<sub>3</sub><sup>-</sup> (CO<sub>3</sub><sup>2-</sup>) pumped into the system during a 1 min period:

$$12.6 \mu\text{mol/L} \cdot 1 \text{ mL/min} = 12.6 \mu\text{mol/min} \quad (1)$$

Quantity of HCO<sub>3</sub><sup>-</sup> (CO<sub>3</sub><sup>2-</sup>) pumped into the system during a 1 h period:

$$12.6 \mu\text{mol/L} \cdot 60 \text{ min} = 756 \mu\text{mol/h} \quad (2)$$

With regard to the time period we may conclude that the electrical conductivity of the effluent remains stable with increasing amounts of OH<sup>-</sup> type AE resin. Furthermore, the increase in the electrical conductivity after 12 h was approximately 1 μS/cm when PNFP was packed with 10 g of the OH<sup>-</sup> type AE resin. The results show that continuous operation for 12 h is possible using the PNFP packed with 10 g of the OH<sup>-</sup> type AE resin. Taking into account other external factors (i.e., the quantity of HCO<sub>3</sub><sup>-</sup> (CO<sub>3</sub><sup>2-</sup>) in the sample), it is recommended to use 20 g of the OH<sup>-</sup> type AE resin.

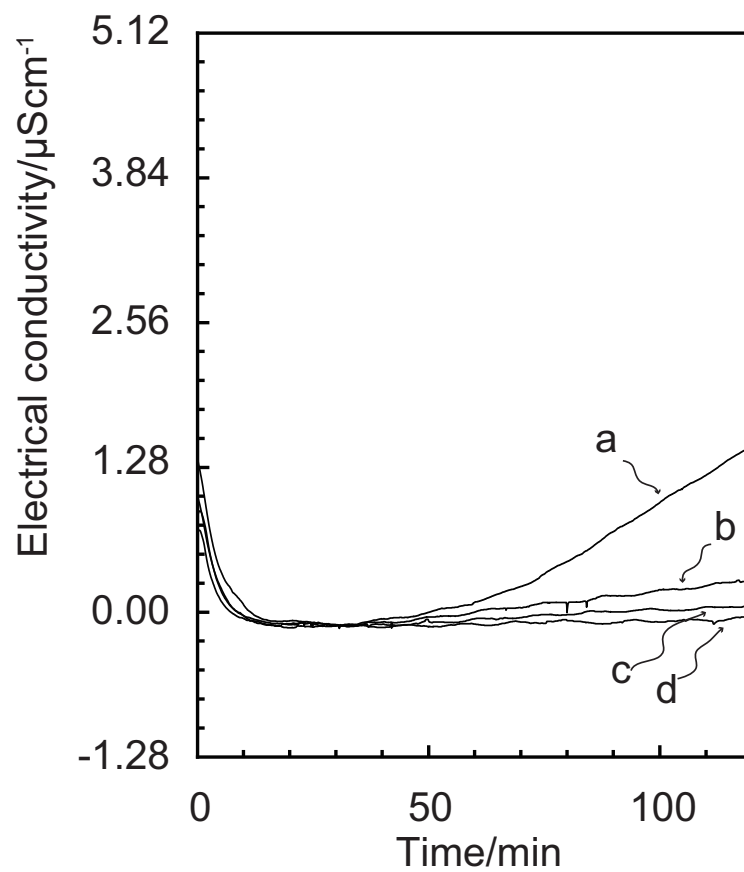


Figure 5.5:  $\text{CO}_2$  adsorption capacity of the dried  $\text{OH}^-$  type AE resin prepared using the proposed method. The numbers indicate the quantity of the  $\text{OH}^-$  type AE resin in the vessel: (a) 1 g, (b) 2 g, (c) 5 g, and (d) 10 g.

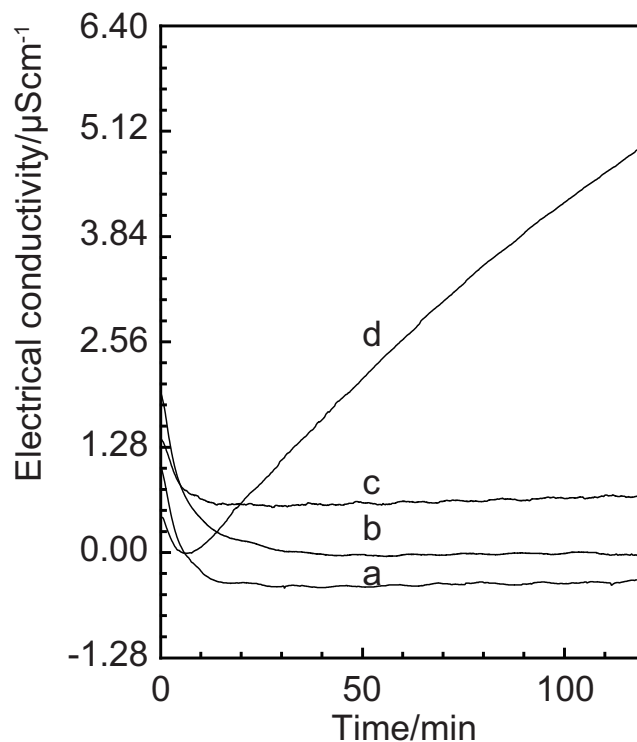


Figure 5.6: Effect of water content on the adsorption of CO<sub>2</sub> gas in the vessel by the CO<sub>2</sub> gas in the vessel. The numbers indicate the quantity of water added to 10 g of OH<sup>-</sup>-type AE resin in the vessel: (a) 1 mL, (b) 2 mL, (c) 5 mL, and (d) 10 mL.

### 5.3.2 Effect of water content in the OH<sup>-</sup>-type AE resin on the adsorption of CO<sub>2</sub> gas in the vessel

We can assume that the quantity of water vapor that passes through the membrane of a GPT is smaller than the quantity of other gases like less than N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, etc. However, it can be expected that the OH<sup>-</sup>-type AE resin packed in the vessel will be wetted by the water vapor. The effect of the water content in the OH<sup>-</sup>-type AE resin on the adsorption of CO<sub>2</sub> gas in the vessel has been investigated by using the system as show in Fig. 5.2. If we accept that the thickness of the water phase formed on the OH<sup>-</sup>-type AE resin surface increases by adding more pure water to the OH<sup>-</sup>-type AE resin, we can expect that the CO<sub>2</sub> concentration in the vessel will increase because the amount of CO<sub>2</sub> dissolved in the pure water is very low. Therefore, the electrical conductivity of the effluent from the CO<sub>2</sub> remover will be increased. Fig. 5.6 shows that the electrical conductivity increases significantly after 5 min when 10 mL of pure water is added to 10 g of the OH<sup>-</sup>-type AE resin. In addition, when the quantity of pure water added to 10 g of the OH<sup>-</sup>-type AE resin packed in the PNFP is equal or lower than 5 mL, the removal of CO<sub>2</sub> in the vessel is prompted and a large portion of the CO<sub>2</sub> gas in the vessel is removed.

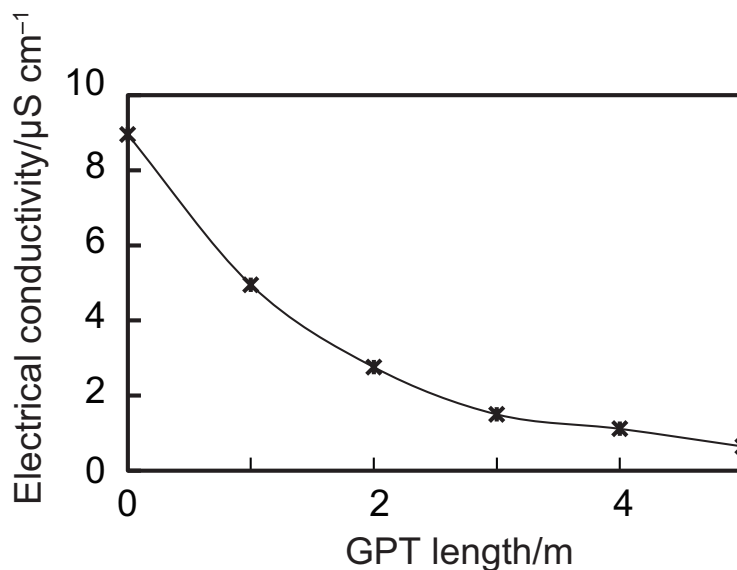


Figure 5.7: Effect of GPT length on the removal of  $\text{CO}_2$  from the suppressor effluent.

### 5.3.3 Effect of GPT length on the removal of $\text{CO}_2$ from the suppressor effluent pumped into the GPT

The effect of the length of the GPT on the removal of  $\text{CO}_2$  from the suppressor effluent was estimated by using the system as shown in Fig. 5.2. Fig. 5.7 shows that the electrical conductivity of the effluent from the  $\text{CO}_2$  remover decreases from 8.95 to 1.11  $\mu\text{S/cm}$  when the GPT length increases from 0 to 5 m. The decrease of electrical conductivity can be declared by a longer residence time in the GPT. When the length of the GPT is greater than 3 m, the electrical conductivity appears to level off. Therefore, a GPT length of 4 m has been used as the operating length in this study. Considering the rate-limiting step for  $\text{CO}_2$  removal in the  $\text{CO}_2$  remover in Fig. 5.7, it should be possible to reduce the length of the GPT by using a thinner tubing and still retain the same level of  $\text{CO}_2$  removal. Unfortunately, a commercial product of the desired grade could not be purchased for the present study.

### 5.3.4 Effects of PNFP and temperature in the vessel on the removal of $\text{CO}_2$ from the suppressor effluent

The effects of the PNFP and temperature in the vessel on the removal of  $\text{CO}_2$  from the suppressor effluent were also investigated using the system shown in Fig. 5.2. As can be seen in Table 5.1, the electrical conductivity of the effluent from the  $\text{CO}_2$  remover with and without the PNFP is 2.42 and 3.5  $\mu\text{S/cm}$ , respectively, and the electrical conductivity of the effluent from the  $\text{CO}_2$  remover with the PNFP at 100 kPa in the vessel is less than that without the PNFP at 7.9 kPa.

In addition, the electrical conductivity of the effluent from the  $\text{CO}_2$  remover decreases from 2.4 to 0.2  $\mu\text{S/cm}$  by increasing the temperature in the vessel from

Table 5.1: Effects of PNFP and temperature in the vessel on the removal of CO<sub>2</sub> from the suppresser effluent

|                                     |     |     |     |     |
|-------------------------------------|-----|-----|-----|-----|
| Temperature ( °C )                  | 50  | 50  | 80  | 80  |
| Pressure (kPa)                      | 7.9 | 100 | 100 | 7.9 |
| PNFP                                | No  | Yes | Yes | No  |
| effluent( $\mu\text{S}/\text{cm}$ ) | 3.5 | 2.4 | 0.2 | 2.4 |

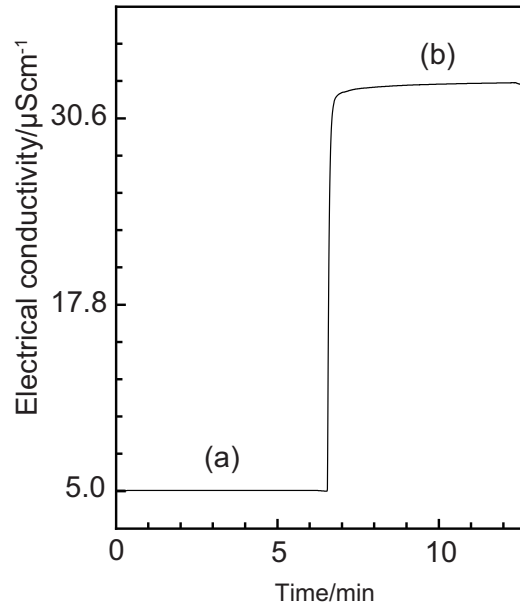


Figure 5.8: Reduction of the electrical conductivity with use of the optimized CO<sub>2</sub> remover: (a) with the device, and (b) without the device.

50 to 80 °C. From these results, we conclude that the CO<sub>2</sub> gas concentration in the vessel achieved with the aid of the PNFP is lower than that without the PNFP, and the equilibrium state between the CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub> is shifted to CO<sub>2</sub> as the temperature in the vessel increases. However, taking into account the operating limit temperature (60 °C) of the resin used in this study, it is recommended to maintain the temperature in the vessel between 37 and 50 °C.

### 5.3.5 Decrease in electrical conductivity and quantity of CO<sub>2</sub> under optimized conditions with the CO<sub>2</sub> remover

The decrease in the electrical conductivity with the CO<sub>2</sub> remover was determined by using the system as shown in Fig. 5.2, Fig. 5.8 shows that the electrical conductivity with and without the CO<sub>2</sub> device is approximately 5 and 30  $\mu\text{S}/\text{cm}$ , respectively. It means a reduction of 80% because the CO<sub>2</sub> gas contained in the suppressed effluent is removed by the CO<sub>2</sub> remover. In addition, a comparison of the graphs shown in Figs. 5.7 and .8 reveal that the electrical conductivity of the CO<sub>2</sub> remover using the type (A) effluent (Fig. 5.8) is five times greater than that

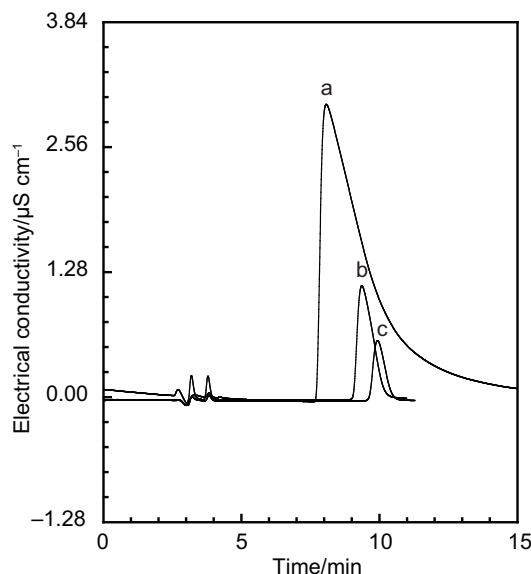


Figure 5.9: Decrease in the quantity of  $\text{CO}_2$  gas with use of the optimized  $\text{CO}_2$  remover: (a) peak area without the device (14051680 a.u.), (b) peak area with the device at 100 kPa and 37 °C (1747208 a.u.), and (c) peak area with the device at 100 kPa and 50 °C (783086 a.u.).

with the type (B) effluent (Fig. 5.7). This result is obtained because the  $\text{HCO}_3^-$  ( $\text{CO}_3^{2-}$ ) concentration contained in the type (A) carbonate buffer solution is approximately five times greater than that the type (B) carbonate buffer solution. The  $\text{CO}_2$  concentration of the system effluent obtained with the system as show in Fig. 5.2 was also determined by injecting the effluent into the ion chromatograph (Fig. 5.4) using an in-line generated pure NaOH solution as eluent. This eluent was generated by the system as illustrated in Fig. 5.3. In Fig. 5.9. we can see that the concentration of  $\text{CO}_2$  contained in the effluent treated by the  $\text{CO}_2$  remover at 37 °C and 50 °C is reduced to approximately one eighth and about one eighteenth (square/square) compared with the concentration obtained without the device. In addition, the quantity of  $\text{CO}_2$  removed by the  $\text{CO}_2$  remover, adjusted at 50 °C is approximately double of the amount of  $\text{CO}_2$  removed at 37 °C. Although the quantity of removed  $\text{CO}_2$  increases with an increase of the temperature in the vessel, the  $\text{CO}_2$  gas in the effluent is not completely removed by the  $\text{CO}_2$  remover due to the dissolution of the  $\text{CO}_2$  gas in the suppressor effluent.

### 5.3.6 Evaluation of IC analysis performance using the $\text{CO}_2$ remover in IC

The performance of the  $\text{CO}_2$  remover was tested by the analysis of anions when a carbonate buffer solution (A type) as an eluent and anion exchange column as an anion analysis was used with the aid of the ion chromatograph as shown in Fig. 5.4 (the other conditions were described in section 5.2.6). It can be seen from the chromatograms of the standard solution of inorganic anions (Fig. 5.10) that

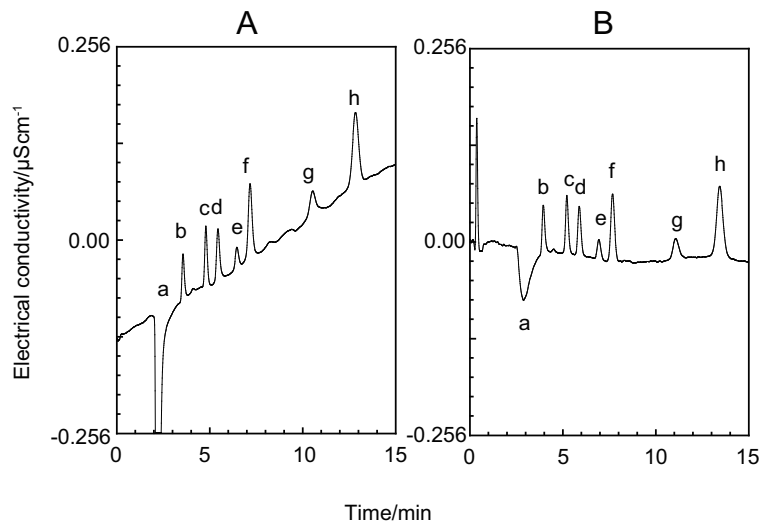


Figure 5.10: Chromatograms of standard inorganic anions. A: without the CO<sub>2</sub> remover; and B: with the CO<sub>2</sub> remover. Samples: (a) water dip, (b) F<sup>-</sup> (50ppb), (c) Cl<sup>-</sup> (100ppb), (d) NO<sub>2</sub><sup>-</sup> (150ppb), (e) Br<sup>-</sup> (100ppb), (f) NO<sub>3</sub><sup>-</sup> (300ppb), (g) PO<sub>4</sub><sup>2-</sup> (300ppb), (h) SO<sub>4</sub><sup>2-</sup> (400ppb).

the base-line drift is smaller with the CO<sub>2</sub> remover, and the signal intensity of the water dip is decreased significantly with the CO<sub>2</sub> remover. Therefore, the anion detection limit achieved in IC instruments with a CO<sub>2</sub> remover is on the order of a few ppb.

## 5.4 Conclusions

All the experimental results presented in this paper were consistent with the described mechanisms. The optimized conditions for the CO<sub>2</sub> remover evaluated in this study were found to include: (1) the use of 10 g of OH<sup>-</sup> type AE resin amount for 12 h of continuous operation, (2) < 5 mL of pure water added to 10 g of the OH<sup>-</sup> type AE resin for the prompt removal of CO<sub>2</sub> in the vessel, (3) an operating temperature between 37 and 50 °C, and (4) a GPT length of 4 m. Under these optimized conditions and by using a carbonate buffer solution (A type), the electrical conductivity of the effluent is dropped to 25 µS/cm, the baseline of the electrical conductivity remains stable and the signal intensity of the water dip is significantly decreased. The detection limit of F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>2-</sup>, and SO<sub>4</sub><sup>2-</sup> were 3.94, 6.52, 11.8, 18.8, 16.6, 21.4, and 56.3 ppb, respectively.

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