



# Fabrication and evaluation of an electro dialytic carbonate eluent generator for ion chromatography



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## ABSTRACT

An electro dialytic potassium carbonate eluent generator and its associated potassium bicarbonate eluent generator have been fabricated for ion chromatography (IC). The device can withstand high backpressure up to ~32 MPa and no observable leakage under such pressure is found during 2 h. In the range of 0–13.7 mM, potassium carbonate concentration can be generated linearly with the applied current with a slope that is essentially Faradaic. At least 10 mM potassium carbonate can be online changed into 10 mM potassium bicarbonate via a potassium bicarbonate eluent generator, which offers an easy way to manipulate the separation selectivity. When coupled with IC system, the device demonstrated good reproducibility indicated by less than 0.52% of the relative standard deviation of the retention times.

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## 1. Introduction

Since introduced in 1975 [1], ion chromatography (IC) in suppressed format has been a well-established technique for the determination of ionic analytes. One of the great developments achieved for modern IC system is the introduction of electro dialytic eluent generator (EDG) [2–4]. In IC, acids and bases (or salts of weak acids) are commonly used as chromatographic eluents. Until the advent of the EDG, eluent preparation was strictly manual. This leads to many problems such as tedious, contamination-prone and subject to operator errors [5]. These drawbacks can be eliminated by using an EDG, which offers users the benefits of simplicity, ease of use, and improved system reproducibility.

The first high pressure EDG was a capillary-scale NaOH EDG [6]. Small et al. [7,8] subsequently reported the use of packed ion-exchange column for electrically generating KOH eluent. Such generator (also called ion reflux) was able to withstand high pressure [8]. A KOH EDG was introduced commercially by Dionex Corp. in 1998 [4]. We have also reported a resin bead-based capillary scale KOH EDG with the configuration of two-membrane [9,10] or single-membrane [11]. More recently, an improved ion reflux device for generation of KOH eluent has been described [12]. All of these reports were based on the generation of KOH eluent. Presently strong base (e.g. KOH) EDG has been widely used for anion analysis in

combination with hydroxide-selective column developed by Thermo Fisher Corp. (well-known Dionex Corp.). Hydroxide eluent is a good one in terms of detection since the suppressed product of hydroxide is nearly pure water, then leading to an extremely low background and thereby much improved signal to noise ratio. While such eluent has rather weak elution ability and gradient operation is always required for anion separation. More important, it is a very harsh eluent and many commercial columns have less stability under such strong alkali solution. Basically they have narrow pH tolerance (e.g. up to pH 12), which mainly results from possible hydrolysis of polymer gel (e.g. polyvinyl alcohol or 2-hydroxypropyl methacrylate) or possible Hofmann degradation of quaternary ammonium groups under strong alkali solution. By comparison, carbonate eluent is relatively mild and has been widely used for the majority of commercial anion columns except Thermo Fisher Corp. Thus there is a need to develop potassium carbonate ( $K_2CO_3$ ) EDG. Although it is claimed that  $K_2CO_3$  EDG has been commercial available by Thermo Fisher Corp. (<http://www.thermoscientific.com/en/product/dionex-eluent-generator-cartridges.html>), there is very limited report for such device even its application. The resin bead-based EDG with two-membrane configuration described in our work was essentially one multiple functional EDG [10], which can generate  $K_2CO_3$  EDG if  $K_2CO_3$  EDG feed solution is provided. While such device can only be applicable to capillary scale IC and its typical flow rate is at  $\mu L/min$  scale, it is not matched with conventional IC system.

Relative to hydroxide eluent, carbonate has much higher elution strength. It offers fast elution while at the other hand easily

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leads to bad resolution for some anions. A solution to address such problem is to use  $K_2CO_3$ - $KHCO_3$  mixed eluent or to modify the pH of  $K_2CO_3$  solution online. Since  $KHCO_3$  is monovalent anion and has much lower elution ability, the elution strength can be manipulated by varying the ratio of  $K_2CO_3$  and  $KHCO_3$ . Such function can also be electrodiagnostically online achieved via a  $KHCO_3$  pH modifier ( $KHCO_3$ -pHM). Such device can be combined with  $K_2CO_3$  EDG to generate  $K_2CO_3$  and  $KHCO_3$  mixed eluent. Herein, we describe the fabrication and evaluation of a  $K_2CO_3$  EDG and its associated component of  $KHCO_3$ -pHM.

## 2. Experimental

### 2.1. Regents and materials

Analyte solutions were prepared in the form of either sodium or potassium salts. Typically, these were analytical grade chemicals, used as received from the vendors. Milli-Q ultra-pure water was used throughout with a specific receptivity of about  $18.3 M\Omega \cdot cm$ . Cation exchange membrane (CEM) and anion exchange membrane (AEM) were from Asahi Glass Public Corp., respectively.

### 2.2. Fabrication of $K_2CO_3$ EDG and $KHCO_3$ pH modifier

The EDG cartridge is the key component of  $K_2CO_3$  EDG. Its schematic diagram is illustrated in Fig. 1. PEEK matched device is used for housing the cartridge, which consists of an eluent generation chamber and  $K_2CO_3$  reservoir, connected together by ion exchange membrane (IEM) connector. The IEM connector contains two sections of CEM section and AEM section, which are fabricated by a stack of six layers of CEM and AEM, respectively. The CEM section is located directly above the cathode and the AEM section is located directly above the anode in the eluent generation chamber. The electrodes are connected with a programmable-control constant current source. To generate  $K_2CO_3$  eluent, pure water is pumped into the eluent generation chamber and a given constant current is applied for the device. Under the electric field, the electrolysis of water occurring at the anode and the cathode produces  $H^+$  plus oxygen and  $OH^-$  plus hydrogen, respectively. Simultaneously,  $K^+$  in the  $K_2CO_3$  reservoir migrates across the CEM section and combines with the  $OH^-$  produced at the cathode to form a KOH solution. In the meantime,  $CO_3^{2-}$  migrates across the AEM section and combines with  $H^+$  produced at the anode to form a carbonic acid solution. Reaction between KOH and  $H_2CO_3$  will form a  $K_2CO_3$  eluent. The concentration of  $K_2CO_3$  formed is directly proportional to the current and inversely proportional to the flow rate of pure water flowing through the eluent generation

chamber.

The  $KHCO_3$ -pHM is essentially a  $KHCO_3$  EDG and its fabrication is as follows. It consists of an eluent chamber packed with cation exchange resin that is fitted with an anode at its outlet. A cathode is put into the regenerant solution channel, which connected through multiple layers of CEMs. When a constant current is applied to the device, controlled amount of  $K^+$  by current are forced to migrate across the CEMs toward the cathode and combine with  $OH^-$  produced in the cathode to form a KOH solution, then going to waste. In the meantime,  $H^+$  generated at the anode converts  $CO_3^{2-}$  into  $HCO_3^-$ . Therefore, the pH of the incoming  $K_2CO_3$  eluent can be modified to form a  $K_2CO_3$ - $KHCO_3$  mixed eluents used for IC by controlling the current. Its schematic diagram is shown in Fig. 1 (right).

When EDG is working, copious amounts of electrodiagnostically gas will be produced, which must be removed. Here gas removal is performed by a segment of gas permeable Teflon AF tube.

### 2.3. Chromatographic system

An IC equipment (CIC-160, SHINEHA Corp., China) was used to evaluate the performance of  $K_2CO_3$  EDG. A PEEK chromatographic pump is used to drive pure water to flow through  $K_2CO_3$  EDG and then online changed into  $K_2CO_3$  eluent. Unless otherwise stated, 1 mL/min of the flow rate was used. An AS20 anion column (Thermo fisher Corp., USA) was used for anion separation. In addition, three kinds of commercial anions columns were also used to evaluate the EDG including 1, Shodex IC SI-52 4E (4.0 mm i. d.  $\times$  250 mm length, Shodex, Japan); 2, SK-gel SuperIC AnionHS (4.6 mm i.d.  $\times$  100 mm length, TOSH Corp., Japan); 3, SHINEHA SH-AC-3(4.0 mm i.d.  $\times$  250 mm length, SHINEHA Corp., China). A homemade electrodiagnostically membrane suppressor (EMS) was used to suppress the eluent, which will be described elsewhere. A conductivity detector (CD) equipped by CIC-160 was used for monitoring the effluent.

### 2.4. Calibration of $K_2CO_3$ concentration and conductivity

The concentration of the generated  $K_2CO_3$  concentration was measured on line by conductivity measurement. The conductivity cell was calibrated with standard  $K_2CO_3$  solution with concentration of 0.5–15 mM. The conductance  $G$  (in  $\mu S$ ) of  $K_2CO_3$  solution could be expressed as a quadratic function of the concentration  $C$  (mM  $K_2CO_3$ ), which used to calculate the concentration of  $K_2CO_3$  generated.

$$G(\mu S) = -1.94 \times C^2 + 245.1 \times C + 46.6, R^2 = 0.9997 \quad (1)$$

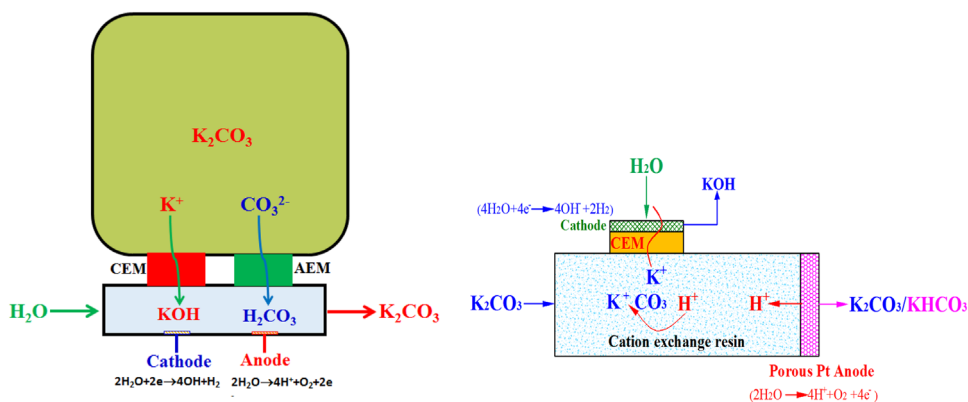


Fig. 1. Schematic diagram of  $K_2CO_3$  EDG (left) and  $KHCO_3$ -pHM (right).

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