



Research article

A gas-free electrodynamic pH modifier for ion chromatography

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ABSTRACT

We for the first time describe a gas-free electrodynamic pH modifier deployed at the pump outlet side to manipulate carbonate eluent used for ion chromatography (IC). It is in sandwich configured, in which the central eluent channel is spatially isolated from two outer regenerant chambers by a stacked cation exchange membranes (sCEM) and a bipolar membrane (BPM) plus a stacked anion exchange membranes (SAEM) (BPM-SAEM), the cation exchange side of BPM is facing the central channel (the cathode direction). One electrode is put in each regenerant chamber and the sCEM side is cathode with respect to the anode of BPM-SAEM side. When a potassium carbonate eluent is pumped into the central channel and a DC current is applied, a controlled amount of potassium ions will be removed by migrating across sCEM into cathodic chamber. Meanwhile, hydronium ions generated from enhanced water splitting at the intermediate layer of BPM will electromigrate into central channel to form bicarbonate. By controlling the current, the potassium carbonate eluent can be manipulated to obtain a mixed eluent with different ratio of carbonate and bicarbonate. At least 10 mM K_2CO_3 eluent can be online changed modified into 10 mM $KHCO_3$ with near-ideal Faradaic efficiency ($\sim 92\%$). The device demonstrated good reproducibility, as indicated by retention time of relative standard deviation (RSD) $< 0.43\%$ and the peak area of RSD $< 0.93\%$.

1. Introduction

Since introduced in 1975 [1], ion chromatography (IC) in suppressed format has been a well-established technique for the analysis of ionic analytes. IC applications are dominated by anion analysis and hydroxide is the preferred eluent from the point of detection, since its suppressed product is nearly pure water, allowing carrying out gradient elution easily and lower limit of detection. Carbonate eluent was used in the firstly commercialized IC system and even today, it is still popular. Relative to harsh hydroxide, carbonate has much stronger elution ability and most anions could be well eluted out during acceptable time under isocratic mode. The eluent strength (and by consequence analysis time) in addition to the selectivity are also changed by varying the bicarbonate/carbonate ratio.

The majority of the preparations of hydroxide eluent is based on electrodynamic production online via an electrodynamic eluent generator (EDG), in which the hydroxide ions are directly produced by water electrodynamic [2]. By contrast, the common preparation of carbonate eluent is manual. During optimization of separation conditions, one needs to prepare carbonate eluents with different concentration or

different ratio of carbonate/bicarbonate. Manual preparation is tedious, prone to contamination and subject to operator errors. Such problems can be solved to a great extent by introduction of carbonate EDG [3,4] or an online pH modifier [5].

It should be noted that even the purest potassium carbonate solution always contains at least three ions (HCO_3^- , CO_3^{2-} , and OH^-) since carbonate is a weak base and an ionization equilibration in the solution exists. Thus, the ratio of HCO_3^-/CO_3^{2-} in the carbonate eluent can be essentially manipulated by modifying the pH of the solution. Potassium carbonate EDG equipped with an electrodynamic pH modifier (EPM) has been commercially available [4]. It is configured with the eluent channel isolated from the outer regenerant chamber via multiple-layers of cation exchange membrane stacked together (sCEM). The anode and the cathode are placed in the eluent and regenerant channel, respectively. Under a given DC current, a controlled amount of potassium ions are forced to migrate across sCEM to the cathode. In the meantime, hydronium ions generated at the anode convert carbonate into bicarbonate. Thus, the pH of the incoming potassium carbonate eluent can be electrodynamic modified to produce carbonate and bicarbonate mixed eluent in anion IC separations. Similar configuration was also described in our previous

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report [6]. A common drawback of these EPMS is that the produced eluent is accompanied with electrolysis oxygen gas that needs to be removed via a degasser, since the anode is immersed in the eluent channel.

Herein we provide for the first time a gas-free EPM that can online modify the pH of the coming potassium carbonate eluent used for anion IC system.

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 resistivity of 18.2 MΩ·cm. Cation exchange membrane (CEM) (Type FKB), anion exchange membrane (AEM) (Type FAA) and bipolar membrane (BPM) (FBM) were from Fumatch Corp. (Germany).

2.2. Fabrication of the gas-free EPM

The fabrication of the gas-free EPM was similar to a two-membrane configuration EDG described previously with some modifications [7]. In brief, the device consists of three compartments, one central eluent and two outer regenerant (Its schematic diagram is provided in Figure 1). 4 layers of AEM (sAEM) plus a BPM stacked together and 5 layers of CEM (sCEM) stacked together (membrane area is 38 mm long × 12 mm wide) are used to isolate the anodic regenerant chamber and the cathodic regenerant chamber from the central channel, respectively. Prior to use, the CEM, BPM and AEM is suggested to be cleaned by immersing in potassium carbonate solution, aiming to remove possible impurity ions. The CEM side of BPM is facing the eluent channel and the AEM side of BPM is contact with sAEM. Both porous platinum screen electrodes are placed in two regenerant chambers, which are in contact with sCEMs and sAEM via a sulfonate functionalized gasket screen and a quaternary ammonium functionalized gasket screen, respectively. Fine cation exchange resins are packed into the central channel, aiming to reduce the electric resistance of the device. Unless otherwise stated, the effluent from the suppressor is used for feeding both regenerant chambers in one direction (co-current flow). Potassium carbonate eluent driven by a high-pressure pump flows through the eluent channel in the opposite direction with the regenerant solution. Alternatively, potassium

carbonate eluent can be produced by a carbonate EDG [3]. Here, the former was chosen to evaluate the EPM. Note: the EPM described here has been demonstrated to modify potassium carbonate eluent, but definitely it can also be applied for sodium carbonate. The former was chosen to be resulting from slightly higher mobility of potassium relative to sodium, and then leading to higher current efficiency. This is also helpful to achieve higher current efficiency of an electroalytic suppressor downstream.

2.3. Chromatographic system

Figure 2 schematically shows the total chromatographic system. An IC equipment (Metrohm 861, Switzerland) was used to evaluate the performance of the device. A high-pressure pump was used to drive potassium carbonate eluent to pass through the EPM, followed by an injector, an analytical column housed in a column oven (35 °C), an anion electrolytic membrane suppressor (AEMS-100, obtained from Minghao Corp., China), and a conductivity detector. The effluent of the detector went to the regenerant chambers of the suppressor, then went to the regenerant chambers of the EPM, finally went to waste.

Two kinds of commercial anion columns were also used here, including Metrosep A supp 5 (4.0 mm i.d. × 150 mm length, Metrohm Corp., Switzerland) and TSKgel SuperIC-AZ (4.6 mm i.d. × 150 mm length, TOSOH Corp., Japan).

2.4. Calibration of carbonate solution

Since carbonate is a weak base and the fractions of concomitant anions (CO_3^{2-} , HCO_3^- and OH^-) vary in different concentration of potassium carbonate solution. Thus, the concentration calibration of carbonate solution cannot be directly carried out by conductivity measurement. Here it was performed by a suppressed IC method, in which either carbonate or bicarbonate can be normalized to be carbonic acid followed by measuring its conductance to establish the calibration curve of conductance and concentration [8].

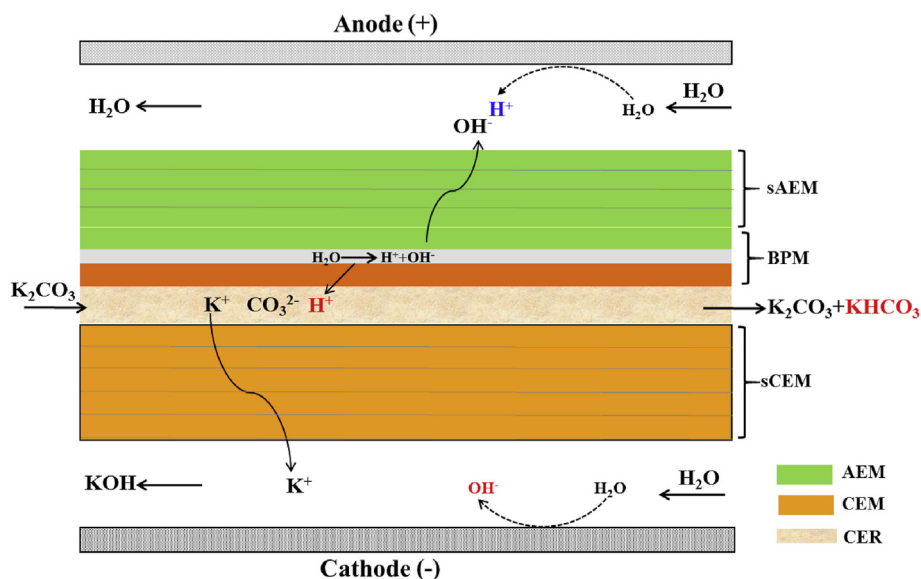


Figure 1. Schematic diagram of gas-free EPM. Note: To show clearly, the scale of BPM is not proportional to its real size.

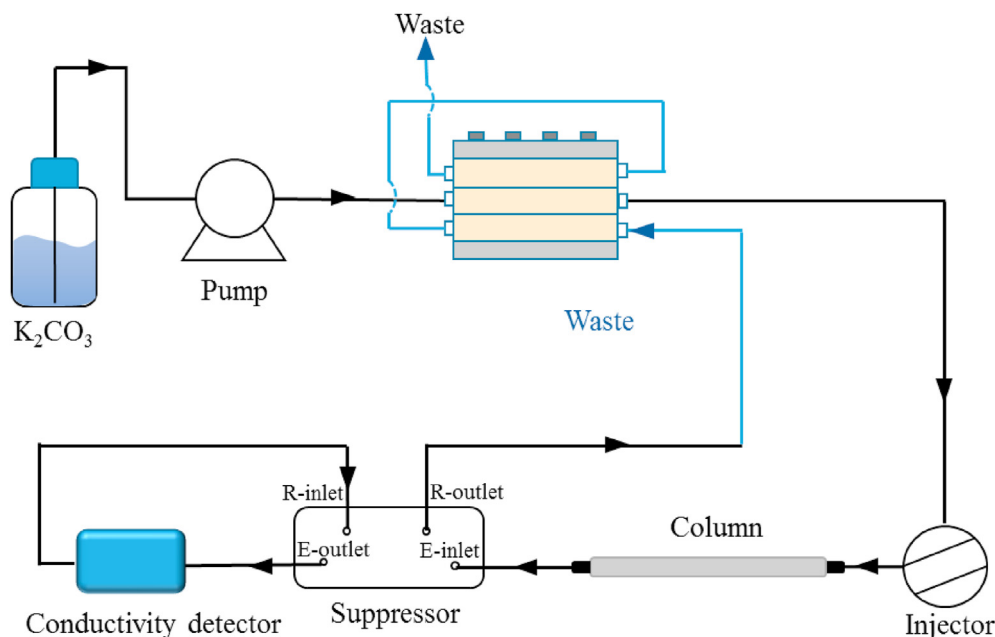


Figure 2. Schematic diagram of the whole IC system.

3. Results and discussion

3.1. Working principle of the EPM

It is known that enhanced water splitting in the interface of BPM will occur under the electric field, then generating H^+ and OH^- [9]. In such process, no hydrogen and oxygen gas are generated, unlike conventional water electrolysis. When potassium carbonate eluent is pumped into the central channel and aqueous solution flows through outer regenerant channels, under the electric field, the hydronium ions generated at the interface of the BPM migrate into central eluent channel to combine with CO_3^{2-} into HCO_3^- (in other words, the pH value of the eluent was modified to be lower). Meanwhile, the displaced K^+ ions in the eluent migrate across sCEM into the cathodic chamber. The net effect is the change of the ratio of CO_3^{2-} and HCO_3^- , then generating a mixed solution of carbonate and bicarbonate with a controlled fraction.

It should be noted that the use of BPM other than CEM to fabricate EPM is to ensure only hydronium ions to be introduced in the eluent channel, otherwise possible impurity cations will be also migrated to the eluent channel together with the hydronium, especially in the case of recycled mode in which the effluent from the electrodiolytic suppressor is used as regenerant solution.

3.2. Pressure tolerance of the EPM

Since the EPM is typically deployed between the pump and the injector in IC system, wide tolerance of the device that can withstand high pressure in typical chromatographic system is necessary. A single piece of BPM or CEM was insufficient to bear high pressure; the maximal pressure that can bear was about 3.5 MPa. To solve it, 4 layers of AEM plus a BPM and 5 layers of CEM stacked together were used for fabricating the EPM. Based on the method described previously [10], the pressure tolerance of the device was tested by plotting the flow rate and the produced backpressure. The fitted plot was found to have good linear relationship (correlation coefficient, $R^2 = 0.9991$) in the tested pressure range up to 22 MPa, as illustrated in Support information (SI)-Figure 1. Under the backpressure of 22 MPa, the terminal exit flow measured with and without the load was found to be almost same. And no observable leakage was found over 1 h-long period, indicating good mechanical

strength of the device and can meet well typical pressure requirement of IC system (<17 MPa).

3.3. Current-voltage behavior of the EPM

The current-voltage behavior of the device under the forward bias (CEM side of BPM positive) was explored, as shown in SI-Figure 2. In the range of 0–2.55 V, the forward current was close to zero, which probably resulted from that no water splitting occurred in such range. When further increasing the voltage, a rapid increase of the forward current was observed. It can be explained by the electromigration of cations and anions, in which hydronium ions from enhanced water splitting of BPM migrated toward the central channel while hydroxide ions migrated toward the anodic regenerant chamber, potassium ions in the eluent migrated to cathodic channel. In the voltage range of 3.81–4.95 V, the fitted line between the applied voltage and the corresponding current showed linear correlation ($R^2 = 0.9982$), and the intersection point of the extension line of the fitted line with X-axis was ~ 3.4 V. The slope of the fitted line, which could be approximately regarded as the resistance of the device, could be computed to be $\sim 60.2 \Omega$. Low resistance is helpful to modify high concentration range of carbonate eluent or may also be useful to reduce Joule heating at lower flows.

3.4. Carbonate eluent composition manipulated by the EPM

The change in potassium carbonate eluent manipulated by the EPM was roughly evaluated by conductivity measurement of the conductance of the eluent; two consecutive runs were shown in Figure 3. The conductivity of the effluent showed almost instant change with the current of the EPM and highly correlation between them was observed.

The mixed eluent of carbonate and bicarbonate is commonly used in anion separation, which is helpful to improve the separation selectivity. Strictly, potassium carbonate itself is a mixed eluent containing carbonate and bicarbonate since carbonate is a weak base and an ionization equilibration in the solution exists. This is true even for the purest potassium carbonate solution. However, the main fraction of carbonate eluent is carbonate and the fraction of bicarbonate is less. For example, according to the method described previously [8], the ratio of bicarbonate/carbonate in potassium carbonate solution with concentration of 3 mM, 5 mM, 8 mM and 10 mM was measured to be 0.22, 0.18, 0.15 and

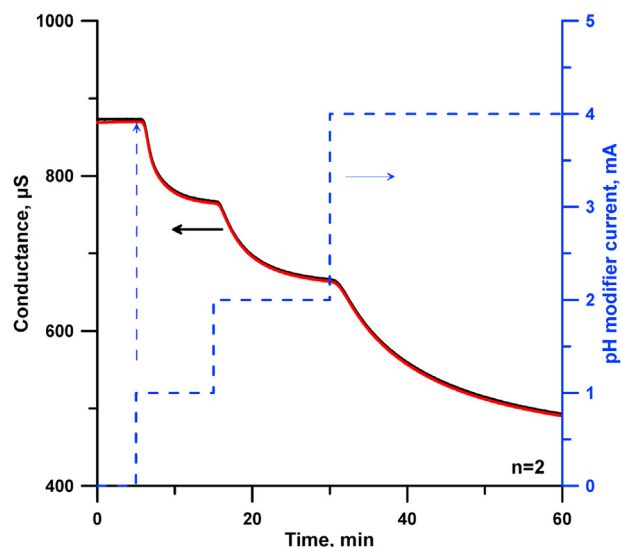


Figure 3. The dependent of potassium carbonate eluent composition on the current of EPM. Conditions: eluent, 3 mM K_2CO_3 ; flow rate of the eluent, 1 mL/min. Note: the composition of potassium carbonate eluent is roughly measured by conductivity measurement.

0.11, respectively. The manipulation effect of the EPM on the fraction of carbonate eluent with different concentration was listed in Table 1. When no current was applied for the EPM, the ratio of bicarbonate/carbonate in different potassium carbonate solutions was less than 0.22. Such ratio could be significantly increased when increasing the current of the EPM. Take 5 mM potassium carbonate eluent as an example, the ratio was 0.18, 0.78 and 42 for the current of 0 mA, 3.2 mA and 8 mA, respectively. 10 mM potassium carbonate eluent could be completely modified to be potassium bicarbonate one when 16.1 mA was applied. Such concentration will be enough to meet the majority of anion separation

requirement. One important thing should be noted that the produced bicarbonate concentration was linear with the current of the EPM. For example, for 10 mM potassium carbonate eluent, the plot of the computed bicarbonate concentration and the applied current of EPM was highly linear, as indicated by the correlation coefficient of 0.9964 (illustrated in SI-Figure 3). The slope of the plot at the typical flow rate of 1 mL/min was 0.574 ± 0.0171 mM/mA, close to the theoretical value of 0.621 mM/mA. These data indicated that potassium carbonate eluent can be readily manipulated by controlling the current applied for the EPM with near-ideal Faradaic efficiency (~92%).

The actual influence of the EPM on the separation of model anions onto two commercial columns was illustrated in Figure 4. The anion column (Metrosep A supp 5, illustrated in Figure 4 left) offered baseline separation towards seven model anions by 5 mM potassium carbonate eluent while the separation resolution was insufficient. When applying the current on the EPM, both the retention time and the resolution increased and much improved resolution was obtained at the current of 2.3 mA. For sole 6 mM potassium carbonate eluent, the other column could not achieve baseline separation for the last two model anions (illustrated in Figure 4 right). The separation resolution could be improved via the EPM and excellent separation resolution could be achieved by the EPM applied at 5.2 mA.

In addition, the utility of the EPM was demonstrated to manipulate the retention of three polyatomic acid anions (as illustrated in SI-Figure 4). Three anions especially for the last one (citric acid) showed obvious dependence upon of the change in pH of the eluent manipulated by EPM.

3.5. Chromatographic performance evaluation of the EPM

To confirm the reliability of the device, a comparison was made by comparing the manually prepared eluent, as shown in Figure 5. For TSKgel SuperIC-AZ column, the optimized condition recommended by the vendor was 1.7 mM K_2CO_3 +6.3 mM $KHCO_3$. The separation carried out under such eluent manually prepared was shown in Figure 5. 8

Table 1. Composition analysis of carbonate eluent manipulated by EPM.

C_T , mM	pH	AVE	$[OH^-]$, mM	$[HCO_3^-]$	$[CO_3^{2-}]$	I, mA	$[HCO_3^-]/[CO_3^{2-}]$		
3.00	/	10.98	/	10.98	0.955	0.539	2.461	/	0.22
3.00	10.34	10.48	10.46	10.43	0.267	1.317	1.683	1.6	0.78
3.00	9.96	9.83	9.87	9.89	0.077	2.192	0.808	3.2	2.71
3.00	8.37	8.35	8.37	8.36	0.002	2.967	0.033	4.8	90.50
5.00	/	11.07	/	11.07	1.175	0.755	4.245	/	0.18
5.00	10.66	10.60	10.65	10.64	0.433	1.627	3.373	1.6	0.48
5.00	10.43	10.43	10.42	10.43	0.267	2.195	2.805	3.2	0.78
5.00	10.18	10.18	10.19	10.18	0.153	2.890	2.110	4.8	1.37
5.00	9.82	9.79	9.79	9.80	0.063	3.840	1.160	6.4	3.31
5.00	8.73	8.70	8.66	8.70	0.005	4.884	0.116	8.0	42.01
8.00	/	11.13	/	11.13	1.349	1.073	6.927	/	0.15
8.00	11.01	11.01	11.00	11.01	1.015	1.365	6.635	1.6	0.21
8.00	10.80	10.81	10.80	10.80	0.636	1.979	6.021	3.2	0.33
8.00	10.64	10.61	10.59	10.61	0.411	2.698	5.302	6.4	0.51
8.00	10.17	10.17	10.16	10.17	0.147	4.699	3.301	9.6	1.42
8.00	9.22	9.27	9.26	9.25	0.018	7.372	0.628	12.9	11.75
10.00	/	11.27	/	11.27	1.862	1.009	8.991	/	0.11
10.00	10.80	10.81	10.81	10.81	0.641	2.459	7.541	3.2	0.33
10.00	10.46	10.49	10.49	10.48	0.302	4.089	5.911	6.4	0.69
10.00	10.35	10.36	10.33	10.35	0.222	4.847	5.153	8.0	0.94
10.00	10.20	10.18	10.19	10.19	0.155	5.743	4.257	9.6	1.34
10.00	9.78	9.75	9.76	9.76	0.058	7.828	2.172	12.9	3.60
10.00	8.63	8.56	8.64	8.61	0.004	9.809	0.191	16.1	51.29

Conditions: flow rate of the eluent, 1 mL/min.

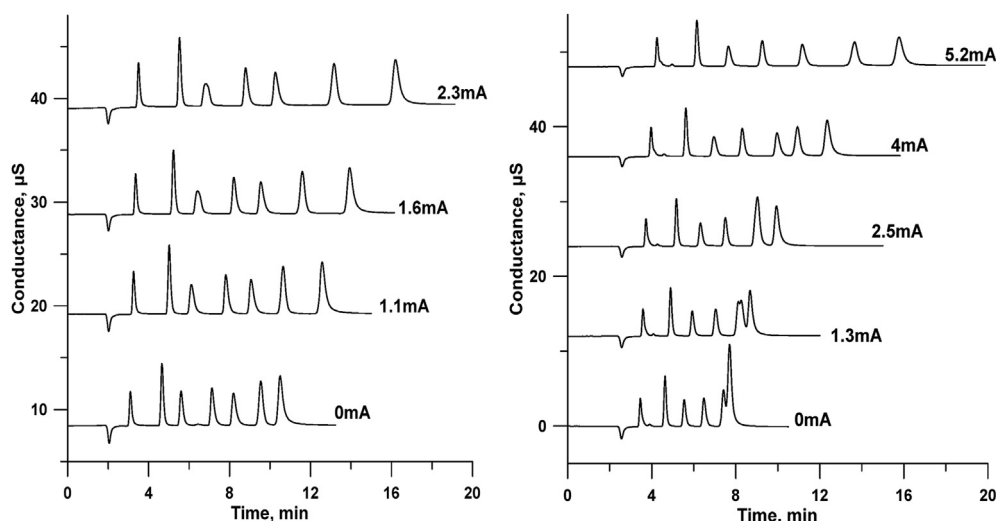


Figure 4. Influence of EPM on the separation of model anions. Conditions: analytes ($100 \mu\text{M}$ except HPO_4^{2-} $200 \mu\text{M}$), F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} ; injection, $25 \mu\text{L}$; Left, column, Metrosep A supp 5; column temperature, 30°C ; eluent, $5 \text{ mM K}_2\text{CO}_3$; flow rate of the eluent, 0.7 mL/min ; suppressor current, 25 mA ; Right, TSKgel SuperIC-AZ; column temperature, 40°C ; eluent, $6 \text{ mM K}_2\text{CO}_3$; flow rate of the eluent, 0.8 mL/min ; suppressor current, 30 mA .

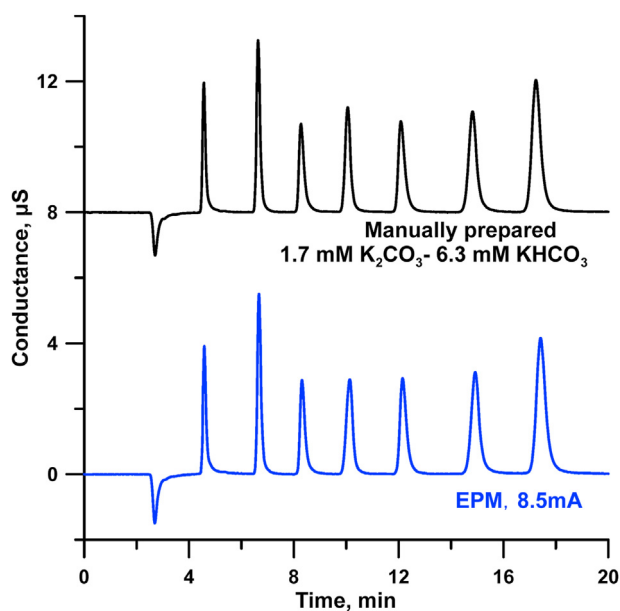


Figure 5. Comparison of the eluent manually prepared and EPM. Conditions: the flow rate of the eluent, 0.8 mL/min ; column, TSKgel SuperIC-AZ; column temperature, 40°C ; suppression current, 30 mA ; manually prepared eluent, $1.7 \text{ mM K}_2\text{CO}_3$ - 6.3 mM KHCO_3 ; EPM modified eluent, $8 \text{ mM K}_2\text{CO}_3$ modified by 8.5 mA . The other conditions same as Figure 4.

$\text{mM K}_2\text{CO}_3$ eluent modified by EPM at 8.5 mA current offered much similar separation effect (Note, this further indicated near-Faradaic efficiency of the EPM). Good retention reproducibility ($n = 3$) was observed in both cases, the relative standard deviations (RSD) of retention time (and peak area) in the range of 0.151 – 0.252% (0.062 – 0.881%) achieved by EPM and 0.031 – 0.119% (0.174 – 0.633%) by manual preparation.

When the EPM was coupled with IC system for anion separation, the total system showed good reproducibility for six consecutive analysis (see SI-Figure 5), as indicated by $<0.43\%$ of the RSD of the retention time, and $<0.93\%$ of RSD of the peak area. Good inter-day reproducibility of three days was also observed, as indicated by $<2.64\%$ and $<3.04\%$ of RSD for the retention time and the peak area, respectively.

The utility of the EPM coupled with IC system was demonstrated by the analysis of inorganic anions in water. The whole system showed good linearity in the concentration range of 0.05 – 10 mg/L (correlation coefficient, $R^2 > 0.99965$ for all analytes). The limit of detection, defined as signal to noise ratio of 3, was ranging from 0.5 – $4 \mu\text{g/L}$. Detailed analytical parameters see SI-Table 1 and the achieved chromatogram was shown in SI-Figure 6. The concentration of model anions determined in the purified water (Wahaha) were $0.098 \pm 0.044 \text{ mg/L}$, $0.218 \pm 0.028 \text{ mg/L}$, $0.308 \pm 0.074 \text{ mg/L}$ and $0.232 \pm 0.082 \text{ mg/L}$ for F^- , Cl^- , NO_3^- and SO_4^{2-} . Their concentrations in the other type of mineral water (Nongfu Spring) were $0.209 \pm 0.073 \text{ mg/L}$, $2.629 \pm 0.031 \text{ mg/L}$, $3.896 \pm 0.109 \text{ mg/L}$ and $6.322 \pm 0.147 \text{ mg/L}$, respectively.

4. Conclusions

This is the first account of an electrolytic pH modifier that does not produce any gas in the produced channel. It is in sandwich configuration and both electrodes are isolated from the central eluent channel. Under electric field, a controlled amount of potassium ions could be displaced by hydronium ions generated by BPM, thus the ratio of bicarbonate/carbonate could be manipulated simply by adjusting the current of the EPM. It is helpful to facilitate the users to develop analytical methods. By slight modification, such device can be used as buffer generator to produce a buffer solution with pH value required; such ramifications will be described in the near future.

Declarations

Author contribution statement

Yue Zhou: Performed the experiments; Wrote the paper.

Yue Sun: Performed the experiments.

Feifang Zhang: Conceived and designed the experiments; Analyzed and interpreted the data.

Bingcheng Yang: Conceived and designed the experiments.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

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