Miniaturized Low-Pressure Ion-Exchange Module and Its Application to an Acidic Eluent Generator for Open Tubular Ion Chromatography

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Abstract

We describe a miniaturized eluent generator (MEG), which can be integrated into open tubular capillary column ion chromatography (OTCC-IC). The MEG consists of one central eluent channel and two feed acid chambers, with each phase isolated by a cation-exchange membrane (CEM) and an anion-exchange membrane (AEM). Pure water flowed through the central eluent channel while acid solution (HA) was fed to both chambers. Applying the electric field to the MEG, H^+ and A^- simultaneously and respectively through the CEM and AEM to form HA in the central channel. The MEG successfully produced tartaric acid and 2,6-pyridinedicarboxylic acid as the eluent for cation OTCC-IC. The gradient elution improved the peak resolution and analytical window for five common cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}).

Keywords Ion-exchange membrane, electrolysis, ion chromatography, eluent generation, open tubular capillary column

1. Introduction

Ion exchange modules are widely used in a pH adjuster and buffer solution generator in flow analysis and an eluent generator and suppressor in ion chromatography [1,2]. Online preparation of the eluents saves time and provides accurate and highly pure chemicals. Electrodialytic eluent generator consisting of a cation-exchange membrane (CEM), anion-exchange membrane (AEM), and/or bipolar membrane improves detection sensitivity and allows for a gradient elution [3-5]. Elkin and co-workers demonstrated a CEM and AEM-based electrodialytic ion reflux device for eluent generation and suppression [6,7]. We reported a low-pressure potassium hydroxide generator in which the eluent channel was separated by the CEM and AEM [8]. This eluent generator was applied to open tubular capillary column ion chromatography (OTCC-IC) and successfully separated five common anions. The OTCC can be used at lower pressures, but the peak resolution is generally lower than that of packed capillary columns. Recently, we applied a partial least squares regression (PLS) to the overlapped peaks in OTCC-IC and FIA for cations quantification [9,10]. The OTCC-IC, in combination with the PLS, was successful in determining the cation concentrations even if their peak resolution was low [9].

In the present study, we fabricated a miniaturized low-pressure ion-exchange module that produces an eluent for cations analysis by OTCC-IC. While the previously reported eluent generator produced potassium hydroxide for anion separation [8],

this paper focuses on cation analysis with tartaric acid (TA) and 2,6-pyridinedicarboxylic acid (PDCA) as the eluent. We describe here the performances of miniaturized eluent generator (MEG) and its application to the isocratic and gradient elution of OTCC-IC.

2. Experimental

2.1. Miniaturized eluent generator

The schematic diagram and photograph of MEG are shown in Fig. 1. The device has a sandwiched configuration, one central
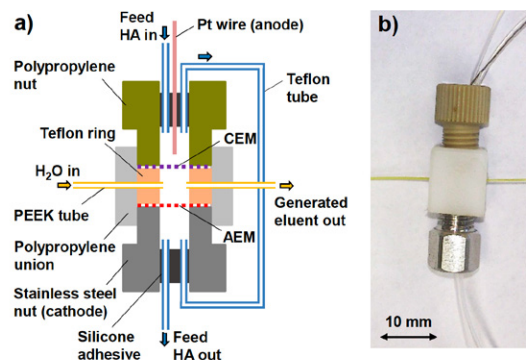

Fig. 1 Miniaturized eluent generator design (a) and photograph (b). HA, acid solution; CEM, cation-exchange membrane; AEM, anion-exchange membrane.

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eluent channel, and two feed acid chambers on both sides. A CEM (24 μm thick in dry condition) and an AEM (20 μm thick in dry condition), supplied by ASTOM Corp., Japan, were used to isolate the central channel and two chambers. Two small holes were drilled into opposite sides of the 1/4-28 threaded polypropylene union at the same vertical location of the Teflon ring (1 mm thick). A PEEK tube (0.15 mm i.d., 0.36 mm o.d.) was inserted in each hole and sealed by epoxy adhesive. A platinum wire (0.3 mm dia., Sanwa Kinzoku Co., Ltd., Japan) inserted in the 1/4-28 threaded polypropylene male nut was used as the anode. A 1/4-28 threaded stainless steel male nut works itself as the cathode. Teflon tubes (0.3 mm i.d., 0.76 mm o.d.) were used for both feed acid chamber in/out connections and held in place with hot-melt silicone adhesive.

Pure water flowed through the central eluent channel while acid solution (HA) was fed to the chamber at the anode side. The effluent from the anode side chamber went to the cathode side chamber. By applying an electric field, H^+ and A^- move simultaneously and respectively through the CEM and AEM to form HA in the central channel. The produced HA concentration was measured online by a lab-made capacitance detector [11], which was calibrated with a standard solution of HA. EVAL-AD7746EB-ND (Analog Devices Inc., USA) was applied to the detector as a capacitance to the digital converter.

2.2. Open tubular capillary column

Preparation of Poly (butadiene/maleic acid) (PBMA) coated OTCC was based on Kuban's method [12]. The fused silica capillary (75 μm i.d. 363 μm o.d., 1 or 5 m long, BGB Analytik USA LLC) was sequentially pretreated with a mixture of 2.5 v/v% hydrofluoric acid and 2.5 v/v% nitric acid, and 1 v/v% hydrochloric acid. The capillary was washed with water and dried with nitrogen gas (N_2, >99.99%, Shikoku Taiyo Nippon Sanso Co. Ltd., Japan). The coating solution (2.4 g PBMA and 0.12 g azobisisobutyronitrile in 10 mL methanol) was filled in the capillary for 5 min and then drained using N_2 (200 kPa). The thin film of the coating solution was left on the capillary inner wall. The treated capillary was quenched for 15 min at 160°C to allow bonding of its surface. These procedures were repeated nine more times to create a 10-layer stationary phase on the capillary inner surface.

2.3. Open tubular capillary ion chromatographic system

The layout of the ion chromatographic system is illustrated in Fig.2. Pure water and acid solution (HA, 5 mM TA or 10 mM
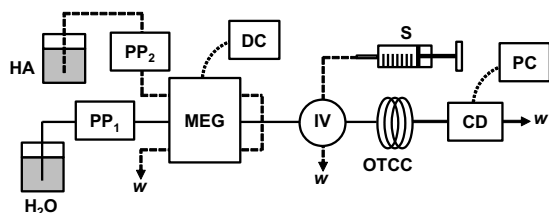

Fig. 2 Open tubular capillary ion chromatography setup. PP1&PP2, peristaltic pump; HA, acid solution; MEG, miniaturized eluent generator; CVG, direct current power supply; IV, injection valve; S, sample; OTCC, open tubular capillary column; CD, capacitance detector; PC, personal computer; w, waste.

PDCA) were delivered to the central channel and electrode chambers of MEG by peristaltic pumps (PP$_1$, OG-RP-400, OGAWA & Co. Ltd., Japan; PP$_2$, RP-1, Rainin Instrument Co., Inc., USA), respectively. A direct current stabilizing power supply (DC, AD-8723D, A&D Co., Ltd, Japan) powered the MEG. The generated eluent went through a 250-nL loop volume injector (IV, CN2-4346EH, Valco Instruments Co. Inc., USA), the PBMA coated OTCC, and then the lab-made capacitance detector (CD) [11]. The detector signals were recorded with a personal computer (PC).

All reagents used in this study were of analytical grade and were used without further purification. Sartorius arium® 611 DI grade deionized water (>18 MΩ cm) was used throughout.

3. Results and Discussion

3.1. Characterization of miniaturized eluent generator

The MEG fabricated is a gas-free, low-pressure eluent generator consisting of three liquid phases (one central eluent channel and two feed acid chambers). Since each phase is isolated by the CEM and AEM, the oxygen and hydrogen gases generated by electrolysis cannot migrate into the eluent channel. Therefore, the MEG does not require a degasser necessary in a two-phase eluent generator [13,14].

The TA concentration generated in the eluent channel was investigated by changing an applied voltage to the MEG in a phased manner. As illustrated in Fig. 3, The MEG generated the constant TA concentration stably at each applied voltages. In gradient elution, a rapid change in the eluent concentration is desired. The rising curve was used to characterize the TA concentration change in response to the change in the applied voltage. The 10% → 90% rise times were calculated to be 1.6 min for 0 V → 1.0 V, 1.3 min for 1.0 V → 1.7 V, 2.5 min for 1.7 V → 2.0 V, and 2.0 min for 2.0 V → 2.2 V. The larger the difference in the generated TA concentration, the longer the rise time tended to be. A 3.8 mM TA of penetration into the central eluent channel
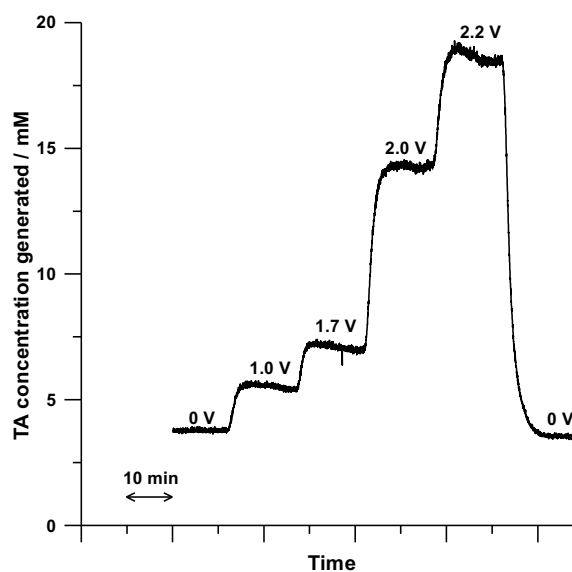

Fig. 3 Generated TA concentration to each applied voltage. Eluent flow rate of water, 1.6 μL min^{-1}; Feed solution, 10 mM TA at 280 μL min^{-1}. The voltages applied to MEG are shown in the figure.

appeared at zero voltage (zero current). The ion exchange between tartrate in the TA feed solution and OH⁻ in the central water channel might occur through the AEM. In addition, the non-dissociated TA (pK_{a1} = 2.98, pK_{a2} = 4.34 [15]) may have permeated the ion exchange membranes and migrated to the eluent channel. This undesirable TA penetration dropped to 1.5 mM when the feed TA concentration was reduced from 10 mM to 5 mM. It is also possible to suppress the TA penetration by applying a reverse voltage to the MEG [8].

3.2. Chromatographic applications

The performance of the MEG was tested with isocratic elution to separate a mixture of Li^+, Na^+, K^+, and Cs^+. Figure 4 shows the chromatograms at applied voltages of 1.1, 1.5, and 1.7 V. Separation of four monovalent cations was achieved. The retention time of each cation shifted toward earlier with increasing applied voltage, *i.e.*, increasing TA eluent concentration. However, divalent cations (Ca^{2+}, Mg^{2+}) could not be eluted from the column with TA eluent.

A PDCA has been used as the eluent for simultaneous determination of monovalent and divalent cations in cation exchange chromatography [12,16]. The PDCA eluent was generated with the MEG and applied to both isocratic and gradient elution to separate a mixture of five common cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}). Figure 5 shows the isocratic and gradient chromatograms with PDCA eluent. Under the isocratic mode (applied voltage: 1.2 V, generated PDCA concentration: 2.5 mM), the peak resolution between Na^+ and K^+ was 0.87, and Mg^{2+} could not be eluted within 90 min. Several gradient programs were tested to improve the Na^+ - K^+ peak resolution and the analytical window for the five common cations (elution duration from Na^+ to Mg^{2+}). The chromatogram for the optimized gradient program (applied voltage: 1.1 V for 0 – 25 min, with a step change to 1.8 V after that) is shown in Fig 5 as the dotted line. Note that
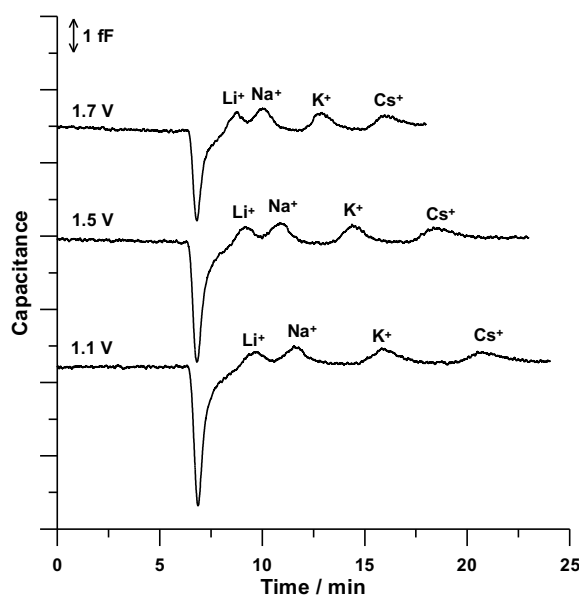
Fig. 5 Isocratic (solid line) and gradient (dotted line) chromatograms performed by MEG, 10 mM PDCA feed at 400 µL min⁻¹. The 75 µm × 5 m PBMA coated OTCC, flow rate 1.6 µL min⁻¹. Sample 100 pmol of each cation in 250 nL. The voltages applied to MEG are shown in the figure.
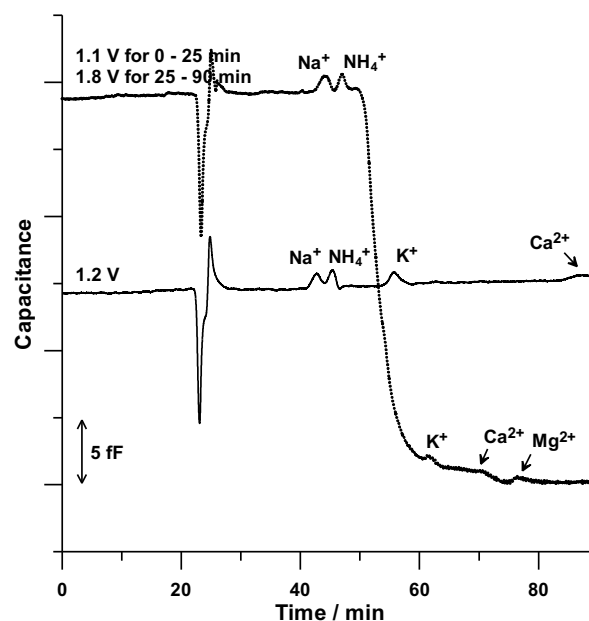
2.3 mM and 8.0 mM PDCA were generated at the applied voltages of 1.1 V and 1.8 V, respectively. The optimized gradient elution improved the Na^+ - K^+ peak resolution to 1.10. In addition, the analytical window for the five common cations was reduced to 34 min, although the background capacitance changed during the gradient run. In the gradient chromatogram shown in Fig. 5, the baseline capacitance decreases even though the eluent TA concentration is increasing. This unexpected decrease is due to a characteristic of the capacitance detector, *i.e.*, the response of the capacitance detector rises linearly with the concentration for low concentration range but reaches a plateau and after that decreases for high concentrations [11].

In summary, we have fabricated the MEG for the online generation of acidic eluents. The TA and PDCA produced by MEG were applied to OTCC-IC to enable the separation of cations. The gradient elution of PDCA successfully improved the peak resolution and analytical window for five cations.

Acknowledgments

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Fig. 4 Isocratic chromatograms performed by MEG, 5 mM TA feed at 8 µL min⁻¹. The 75 µm × 1 m PBMA coated OTCC, flow rate 0.8 µL min⁻¹. Sample 50 pmol of each cation in 250 nL. The voltages applied to MEG are shown in the figure.

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