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Autonomous, waste-free eluent generation and suppression in a single device: Electrodialytic eluent reflux for ion chromatography

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ABSTRACT

Eluent reflux provides a new approach to suppress and reflux (recover) eluent without the continuous generation of chromatographic waste. The current work utilized a device containing ion exchange membranes at the electrodes, in order to prohibit electrolysis gases from entering the eluent stream. Two resin beds (separated by a membrane stack) were responsible for suppressing incoming eluent and regenerating the suppressed eluent to nearly its original concentration after detection. A greater than expected dilution in the eluent concentration was observed as a result of the minor leakage of potassium ions through the anion membrane stack into the electrode chamber. The incomplete recovery of the eluent was offset by the addition of a three port valve (DRV) to regulate eluent concentration. Over 48 h of continuous operation (192 injections), the device's performance was stable (RSD of 0.21% with the three port valve, compared to RSD 3.73% without). The device was able to operate for up to four weeks using 1 L of eluent. Chromatograms showing the reproducibility of the device are presented for anions.

1. Introduction

Electrodialytic ion exchange devices have been the driving force for state-of-the-art ion chromatography for over 20 years. In modern ion chromatography (IC), electrodialytic devices are used for eluent generation [1–3], eluent purification [4], eluent regeneration [5] and the important technique of eluent suppression [6,7]. Electrodialytic devices are also used for sample pretreatment, water purification, and most recently as a charge detector [8].

The use of electrodialytic devices for eluent generation was originally developed by Dasgupta et al. [9]. Their research first demonstrated the ability to generate sodium hydroxide eluent by using water as the pumped phase and controlling the current electronically [9,10]. Electrodialytic eluent generators have been commercially developed based upon this work. These eluent generators use a concentrated liquid form of eluent, such as sodium or potassium hydroxide for anion analysis or methanesulfonic acid for cation analysis. The concentrate is isolated from the pumped phase (water) via a multi-layer ion exchange membrane stack. Eluent counterions from the concentrate are drawn through the membrane stack into the eluent generation chamber by electrodialysis, where they combine with the eluting ions, forming the eluent. This process enables the production of high purity eluent by controlling the current through the device. These types of eluent generators are capable of operating against the backpressure of the analytical column (typically 1500–4000 psi), but also generate electrolysis gas (hydrogen or oxygen) in the eluent flow stream. Hydroxide eluents in IC are a popular choice because they can be produced with high purity, are gradient compatible and can be suppressed to water; this results in low background conductivity and thus greater sensitivity. The combination of commercially available electrodialytic high pressure eluent generators and electrodialytic suppressors has advanced IC instrumentation to a new level of performance and ease of use.

Though electrodialytic techniques have drastically changed the practice and capabilities of IC, none of these approaches have solved the problem of waste generation. During suppression for anion analysis, cations are transported from the suppressor eluent channel to the electrode chambers, continually generating hydroxide waste [6]. Therefore, the proper disposal of accumulated waste is necessary. Several commercialized products have previously been developed to address this issue. One approach was to reduce column diameter to capillary dimensions (Dionex ICS-5000+Reagent-Free HPIC System). This decreased the rate of eluent consumption and waste production to μL min^{-1}. However, capillary systems do not have the same flexibility and robustness of conventional IC systems. Another technique, referred to as eluent regeneration, was configured to direct the suppressor waste

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through a series of purification steps and back to the eluent reservoir, recovering the original eluent [11]. Because the eluent was exposed to the electrodes, where electrolysis gases are evolved and electrochemical byproducts are formed, additional purification steps were required [11]. The electrochemical byproducts, in particular, can be detrimental to the analytical column [4,12]. In the commercial implementation of eluent regeneration for anion analysis, only carbonate eluents were supported and the system was not gradient compatible. While these techniques successfully reduced waste generation, there are limitations to both of them.

In research conducted by Small [13] a technique termed ion reflux was described. Ion reflux completely eliminated the problem waste generation through the use of an electrolytic device. This technique used a single polarized ion exchange resin bed to generate eluent, suppress it and recapture the eluent counterions. In ion reflux, the eluent counterions (i.e. potassium) are initially bound to the cation ion exchange resin. In the case of potassium, water is pumped into a polarized resin bed at the cathode inlet. There, potassium ions from the cation ion exchange resin combine with incoming hydroxide from the cathode, forming potassium hydroxide. Hydronium ions from the anode electromigrate toward the cathode and eventually meet potassium hydroxide, establishing a potassium–hydronium boundary [5,13]. The continuous production of hydronium from the anode keeps the potassium from leaving the resin bed, and thus the potassium is conserved or refluxed, eliminating waste.

An additional advantage to ion reflux is that a single resin bed can act as the eluent generator, separator and suppressor using only water as the pumped phase [13]. However, as was seen in eluent regeneration, the original implementation of ion reflux also resulted in the exposure of eluent to electrolysis gases and electrochemical byproducts. In ion reflux, the anode and cathode are porous platinum discs that serve two functions: acting as the electrodes and retaining the resin in the device [5]. Since the eluent passes through the electrodes, electrolysis gases and electrochemical byproducts enter the eluent stream. The presence of electrolysis gases in the eluent was remedied by placing, sufficient backpressure at the conductivity cell outlet. This minimized the interference during detection. The electrochemical byproducts, however, cannot be removed before analytical column, serving as the main limitation of this technique.

The goal for this study is to investigate compact, electrodialytic devices that are compatible for measuring environmental contaminants in the field. In this paper, we describe an electrodialytic device that generates eluent isocratically, while suppressing and conserving the eluent counterion, in addition to the pumped phase. In this device, electrodialytic ion-exchange occurs through two membrane-separated resin beds, integrating suppression and eluent generation [4]. This device is capable of using recovered eluent in the analytical stream. Additionally, the device isolates eluent flow from the electrode chambers, eliminating the presence of electrolysis gases and electrochemical byproducts from the analytical stream. The design of this device differs from other electrodialytic devices by combining the use of gas-free membrane technology with an integrated eluent generation, suppression, and recovery technique. The authors describe this integrated approach as eluent reflux. Eluent reflux was investigated in this paper because it is a robust and field applicable technique that also addresses some of the limitations of earlier electrodialytic devices.

2. Principles of eluent reflux

2.1. The electrodialytic device

While the process of electrolysis occurs in all electrolytic devices, the process of electrodialysis occurs only in electrolytic devices that contain ion exchange membranes. In electrodialysis, ions from electrolysis are transported across the membranes when

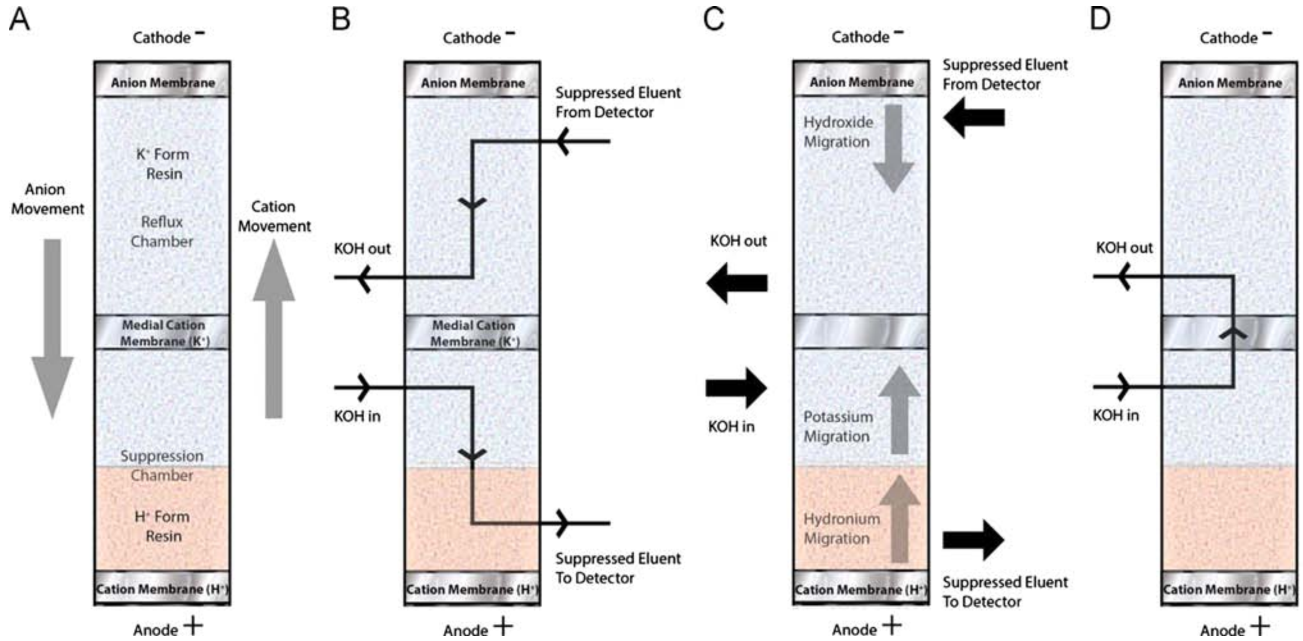

Fig. 1. Block diagram of an ERD. General ion movement and device layout is shown in (A). The medial cation membrane splits the resin bed into the suppression and reflux chambers. The anion membrane stack at the cathode and cation membrane stack at the anode isolate the electrodes from the resin beds. A simplified fluid flow path is shown in (B). KOH flow against cation electromigration forms the basis for suppression. (C) shows electromigration with respect to the fluid flow path. KOH constantly flows toward the anode, opposite the continuous migration of hydronium from the anode, which maintains the H^+–K^+ boundary. (D) shows the simplified net movement of K^+ ions. The constant influx of hydronium into the suppressor bed displaces K^+ ions to the reflux chamber. Here K^+ pairs with incoming OH^- from the cathode forming KOH. The combination of electromigration and the device flow path for the basis for eluent reflux.

a potential is applied. Various electrodialytic devices and their conductive properties have been presented in previous works [5,13–17]. In particular, Small [5] has reported on the use of packed ion exchange resin beds as eluent generators, and Yang [18] has shown how the addition of membranes into an electrolytic device can provide a gas-free, efficient method of eluent generation. Both of these techniques are utilized in eluent reflux.

In an eluent reflux device (ERD), ion transport occurs through a series of resin beds and membrane stacks. A schematic of an ERD is shown in Fig. 1. Fig. 1A, shows the how the placement of two membrane stacks separate the resin beds from the electrode chambers and a third medial membrane stack separates the suppressor and reflux resin beds. Applying a potential to the device causes the electrodialysis of ions in the resin beds from the electrode chambers. Hydronium ions produced at the anode by the electrolysis of the regenerant water electromigrate through the cation exchange membrane stack into the suppressor resin bed. Potassium ions in the suppressor resin bed are subsequently displaced from the resin, causing them to electromigrate toward the cathode. The same process occurs for hydroxide, though the Donnan barrier of the medial cation membrane impedes complete migration. Because of the applied field, ions move independently of the eluent flow as shown in Fig. 1C. The ability of ions to move independently of the eluent flow provides the foundation for eluent reflux.

Ion transport across the membranes provides the counterion source for eluent generation and suppression in an ERD. Fig. 2 shows how the combination of flow and ion movement through multiple membrane-separated chambers enables the device to both suppress and generate eluent. Unlike eluent generation, a concentrated eluent source is not needed on one side of the membrane. The refluxing of potassium across the medial cation membrane provides the source of eluent counterions. Additionally, the electrodialysis of hydronium establishes a potassium–hydronium boundary, which maintains the suppression capacity of the suppression chamber. Because electrolysis is stoichiometric, each hydronium ion electromigrating into the suppressor bed is countered by one hydroxide ion electromigrating into the reflux chamber (Fig. 1A). This in turn causes each potassium that is displaced by hydronium to electromigrate into the reflux chamber where pairs with hydroxide and can be swept away in the eluent flow. Once the potassium–hydronium boundary is established, eluent generation and suppression is almost completely autonomous.

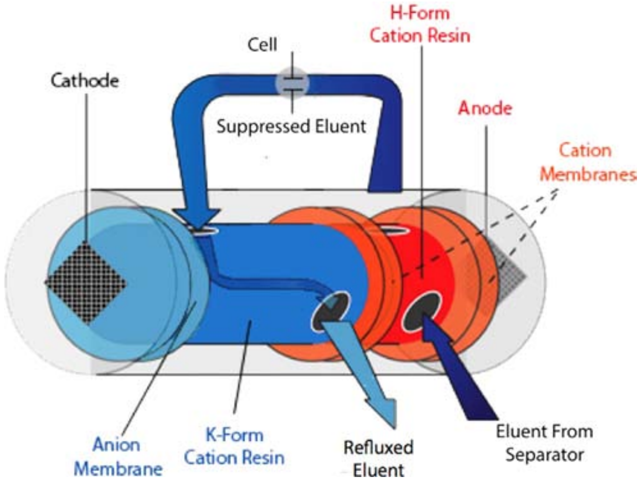

Fig. 2. Schematic of an ERD. The eluent enters the suppressor where the electric field forces potassium toward the cathode. The potassium ions displace hydronium from the resin, which then pair with the excess hydroxide forming water. Electrolytically formed hydronium flowing in from the anode displaces potassium ions from the suppressor resin, which electromigrate toward the medial cation membrane. The combination of hydronium electrodialysis into the suppression chamber and potassium electrodialysis into the reflux chamber maintain the H^+–K^+ boundary. The newly formed water and subsequent anion analytes leave the suppressor and pass through the conductivity cell. Upon entering the reflux chamber, excess hydroxide electrolytically produced at the cathode, combines with the potassium ions electromigrating across the medial cation membrane forming nearly the original concentration of KOH that entered the suppressor.

2.2. Membrane separated chambers

Membrane separated chambers serve two functions: providing a pathway for ion transport and isolating the analytical stream from the electrodes. As seen in Fig. 2, the addition of a membrane stack at each electrode chamber-resin boundary seals the eluent system from electrolysis gases and electrochemical byproducts. Unlike in ion reflux, where the electrodes contact the eluent, the ERD completely isolates the electrodes from the analytical path. The membrane stacks at the electrodes permit ions to electromigrate into the resin while keeping electrolysis gases and electrochemical byproducts from entering the eluent stream. Isolating the electrodes from the analytical stream eliminates the need for any purification steps to remove electrochemical byproducts. Additionally, there is no need for a flow restrictor coil at the conductivity cell outlet to deal with the electrolysis gases.

The main difference between eluent reflux and regeneration is the addition of the reflux chamber, which is formed by adding the medial membrane stack, as seen in Fig. 3. The isolation of the two resin beds with the medial membrane stack allows potassium to electromigrate from the suppressor chamber to the reflux chamber. Hydroxide ions from the cathode electromigrate toward the medial membrane stack where they pair with the incoming potassium ions to form KOH (Fig. 1C). The newly formed KOH is then swept out of the device via fluid flow (Fig. 1B). In eluent reflux, the exiting eluent is the same concentration as the incoming eluent with the exception of some electrodialytically formed water. Through this process, the potassium ions are refluxed or conserved (Fig. 1D).

2.3. Regulating eluent concentration and purity

In IC, eluent dilution can significantly affect retention times. This is particularly true when using hydroxide eluents for anion IC. Ion exchange selectivity would predict that trivalent phosphate ions have a cubic relationship to monovalent hydroxide. In practice, this would mean that any change in hydroxide is multiplied three times for phosphate. For example, if the concentration of hydroxide is halved, then phosphate retention time increases by a factor of nine. There are multiple pathways for dilution, including electrodialytic water formation, sample loop loading and Donnan leakage.

Electrodialytic water formation is a process unique to eluent reflux. In eluent regeneration, the regenerant and eluent water source is the same. In contrast, the sources are completely separated in eluent reflux (Figs. 3 and 4). As stated earlier, the regenerated eluent is nearly the same concentration as the original eluent; therefore, minute differences in the recycled eluent concentration can accumulate and shift retention times. In electrodialytic devices that use a separate water source for the production of hydronium and hydroxide, such as the ERD, there is a minor addition of water via electrodialysis [19]. The addition of water that is produced is proportional to the applied current, as shown in Fig. S1. While this volume is minimal, it can dilute the eluent over time, especially when using a small eluent reservoir volume.

In addition to electrodialytic water formation, dilution of eluent also occurs during sample loop loading. For each injection, the sample loop volume of KOH eluent is lost when the valve switches.

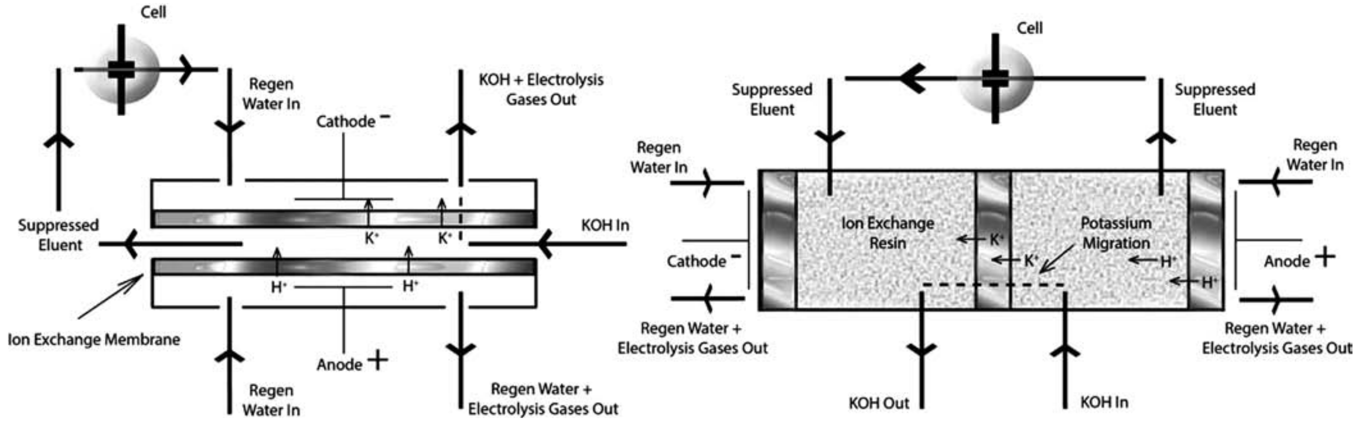

Fig. 3. Flow diagram of a suppressor in eluent regeneration mode versus an ERD. A traditional electrolytic suppressor operated in eluent regeneration mode, is shown in (A). (B) shows an eluent reflux device. In the traditional suppressor, the eluent passes through the electrode chamber, whereas in the ERD it does not. In ERD the eluent and the regenerant water sources are different. Conventional electrolytic membrane suppressors use the same water source for both eluent generation and regeneration.

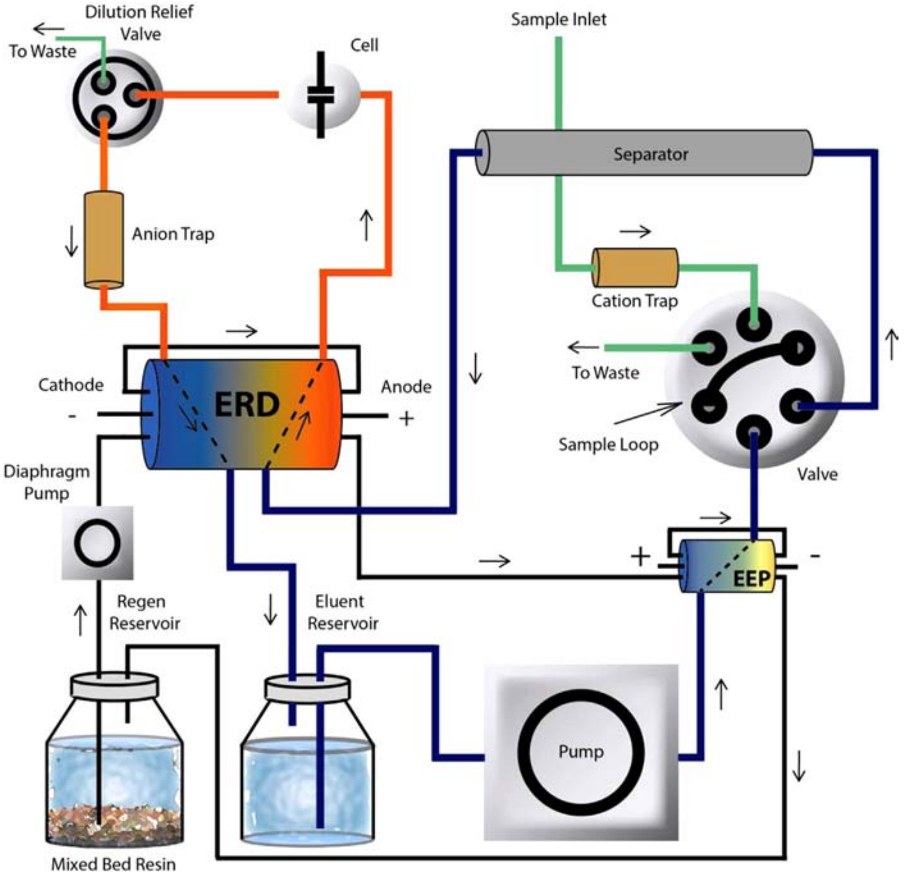

Fig. 4. System configuration. Two separate reservoirs are deployed. The eluent source supplies KOH to the system for analyses (in blue). Suppressed eluent is shown in orange and the green lines represent flow to and from the outside. The regenerant source supplies water to the electrodes (in black). Arrows denote the flow direction. The DRV removes water from the system to maintain a precise eluent concentration. Dashed lines in the eluent reflux device (ERD) and electrolytic eluent purifier (EEP) represent the general fluid flow direction. The polarity of the devices indicates the direction of electromigration with respect to flow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Numerous injections cause retention times to shift as KOH is continually removed from eluent reservoir.

Thirdly, dilution can occur by ion leakage through the anion membrane. Some potassium has the potential to overcome the Donnan barrier and leak into the cathode chamber as a result of water splitting (discussed below).

In order to counterbalance the effects of dilution and maintain the eluent concentration, a dilution relief valve (DRV) is used to remove excess water from the system. The DRV is placed between the detector outlet and reflux chamber inlet to divert suppressed water flow (Fig. 4). This method allows for the purging of a precise volume of eluent-free water from the system, which maintains the concentration of KOH in the eluent reservoir. Though removing water by diverting flow from the analytical system reduces the reservoir volume over time, it more importantly keeps analyte retention times stable.

To regulate eluent purity, an electrolytic eluent polisher (EEP) is used primarily as a carbonate removal device in order to maintain a stable background conductivity. Flow through the EEP is oriented such that anion electromigration is opposite the fluid flow. This configuration maximizes the removal of carbonate and any anionic contaminants from the eluent between the pump and the injection valve. As with all hydroxide eluents, a stable background conductivity is paramount. Because the potassium hydroxide eluent is prepared prior to usage, carbonate contamination is inevitable. The EEP, (Fig. 4), is essentially a 4 × 10 mm electrodialytic anion exchange packed resin bed. Both electrodes are isolated from the anion resin bed by an anion membrane stack, which allows hydroxide ions to continuously regenerate the resin bed and remove impurities. Using the EEP to minimize ambient carbonate in the eluent also plays a role in the stabilization of the peaks. Similar to changes in the hydroxide concentration, the addition of a small concentration of divalent carbonate can have a significant effect on analyte retention times.

2.4. Water splitting

Water splitting is the direct dissociation of a water molecule, which is distinctly different from electrolysis, a redox reaction. In electrolysis, electron transfer drives redox half reactions; yet, only the dissociation of a single water molecule occurs in water splitting. When a potential is applied, the typical dissociation of water can increase by several magnitudes of order [20–24]. Onsager first quantified water dissociation rates under an applied field. While it was observed that the applied field increased dissociation rates, it had no effect on the recombination rates [22,23]. The rate of water splitting is dependent on both the surface area, in which the different ion exchange materials are contacting each other, and the applied current (Fig. S1). Though quantifying the exact rate of water splitting is not a trivial task, sub faradaic behavior in electrodialytic devices is a typical indication of water splitting. When cation and anion exchange material are sufficiently close enough to one another a portion of the applied current is lost to electrostatic interactions.

In the ERD, water splitting occurs at the interface of the anion membrane and cation exchange resin. This is seen in the ERD, where the experimental current needed to produce a given concentration of KOH is slightly higher than theoretically predicted. Because of this, excess current is used in the ERD to ensure that the KOH eluent is fully suppressed. Using excess current in the ERD is not problematic because the current governs the suppression rate. If the suppression rate is maintained, then the generation of eluent inherently follows. In devices where the applied current controls the eluent concentration, such as ion reflux, subfaradaic behavior would affect the device's performance.

3. Experimental

The ERD and EEP (machined from PEEK) were built using Dowex 200–400 mesh resins, and Excellion ion exchange membranes (Snowpure LLC, San Clemente, CA). High resolution images of the ERD and EEP can be seen in Figs. S2 and S3. The ERD and EEP were placed into a typical chromatography system (Fig. 4) including a custom 4 × 100 mm separator column packed with Dionex AS-11 anion exchange latex coated resin (Dionex Corp., Sunnyvale, CA). The system consisted of a CDM-1 conductivity detector (Dionex Corp., Sunnyvale, CA), 6 port, high pressure injection valve with 20 µL sample injection loop (VICI Valco Instruments Co. Inc., Houston, TX), low pressure 3-port solenoid isolation or dilution relief valve (DRV) (Bio-Chem Fluidics, Boonton, NJ), and a Series-1 high pressure pump (Scientific Systems Inc., State College, PA). Forty five grams of mixed bed resin were placed in 200 mL of DI water to remove any contaminants that may migrate through the electrode membranes and into the recycled water regenerant. The bottle was then connected to the electrode chambers to serve as the electrolysis feed water, which was pumped via a diaphragm pump (KNF Neuberger AB, Stockholm, Sweden). The entire system was controlled via a Parallax Propeller microcontroller (Parallax Inc., Rocklin, CA) with software written in house. The Propeller's multiple core processing provided a low power high accuracy option for the simultaneous control of the entire system.

4. Results and discussion

4.1. Device performance

The two most important aspects to consider when determining the performance of an IC system are its reproducibility and reliability. The eluent reflux device (ERD) was tested to determine long-term stability with respect to retention time changes and analyte peak area.

The first test was done in the simplest configuration, using a 180 mL eluent reservoir of 16 mM KOH and no dilution relief valve (DRV). During the run time, the ERD current was 23 mA (21 V) and the electrolytic eluent polisher (EEP) was 5 mA (5.0 V). The eluent and regenerant water flow rates were 0.5 mL min^{-1}. Twenty microliters of anion standard were injected once every hour or six per eluent cycle. Fig. 5 shows the phosphate peaks recorded over nine complete cycles of the eluent reservoir, where one cycle represents 6 h of run time. Though all of the chromatographic parameters were maintained, the eluent concentration was decreasing, as indicated by an increase in phosphate elution time.

Without the DRV, retention times for phosphate were expected to increase at a rate based on the electrodialytic addition of water and the removal of potassium via the sample injection loop. This was calculated using the following two equations:

$$\text{Volume of water from electrodialytic addition } (\mu L\ \mathrm{h}^{-1}) = 60(0.44\ (\mathrm{mA}) - .0272) \tag{1}$$

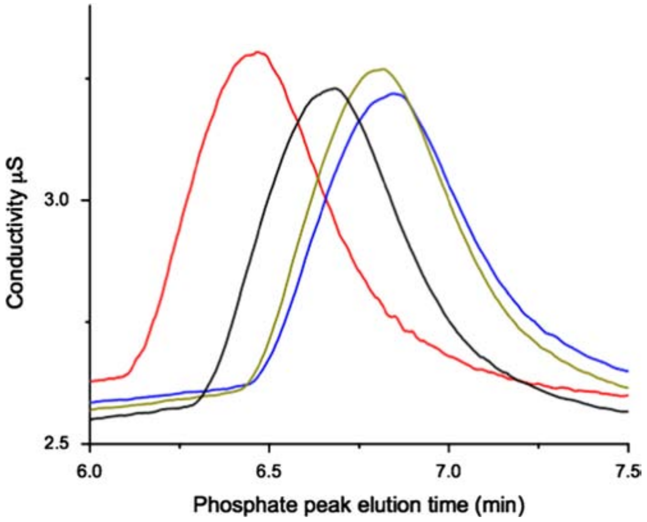

Fig. 5. Phosphate retention time through six eluent cycles w/o DRV. Column: 4 × 100 mm Dionex AS11, Eluent: 16 mM KOH, Flow rate: 0.50 mL min^{-1}, Injection volume: 20 µL, Standard: 7.35 mg L^{-1} phosphate, red: cycle 1 + 150 nS cm^{-1}, black: cycle 5 + 100 nS cm^{-1}, green: cycle 8 + 50 nS cm^{-1}, blue: cycle 9. Without the dilution relief valve (DRV), the concentration of KOH could not be maintained. The influx of water into the system via injections and Donnan breakdown continuously diluted the stock eluent. The RSD of the phosphate peak elution time between the first and eighth cycles (48 h of operation) was equal to 3.7%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$\text{Dilution rate } (\mu\text{L h}^{-1}) = \text{ERD addition} + \text{Loop volume}(\#\text{ of injections h}^{-1}) \qquad (2)$$

Theoretically, the volume of electrodialytically formed water is equal to the equation of the line in Fig. S1 at the applied current, multiplied by 60 min. Therefore, the dilution rate of the system would then be equal to the sum of the ERD electrodialytic water addition, and the injection rate and volume, assuming no water splitting occurs. The EEP, though polarized, is not considered in this equation. Since it contains only anion exchange material, there is no hydronium electrodialysis. Hydroxide enters the device through the cathode and flows through the entire device forming water in the anode electrode chamber.

After 48 h of run time or eight cycles, the retention time for phosphate had steadily increased (RSD = 3.7%). The expected rate of dilution in eluent concentration was 108 µL h^{-1}, while the experimentally measured rate was 1.34 mL h^{-1}. This was determined by the relative standard deviation (RSD) of the phosphate peak with respect to the expected dilution rate. To account for the additional dilution, the conductivity of the regenerant water was measured. The conductivity of the regenerant water exiting the ERD cathode was 36 µS cm^{-1} during operation (background of 0.3 µS cm^{-1}), which corresponded to 0.13 mM KOH. Regenerant water samples were taken and measured for potassium by inductively coupled plasma (ICP). ICP analysis confirmed that potassium ions were passing through the anion membrane stack into the regenerant water at a concentration of 5.1 mg K$^+$ L^{-1}.

The ERD was then tested to see if 16 mM KOH was at a concentration high enough to overcome the Donnan barrier. Sixteen milliliters KOH were pumped through an open circuit system until the conductivity values at the inlet and outlet of the reflux chamber were equal. After the system stabilized, the regenerant water was measured at a value of 0.3 µS cm^{-1}, indicating no failure of the Donnan barrier. When the circuit was closed and driven at 23 mA, potassium leaking resumed. This confirmed that the electric current provided a sufficient force to overcome the Donnan barrier.

To counterbalance the loss of potassium from the eluent reservoir, the DRV was added and set to remove water from the system at a rate of 1.34 µL h^{-1} during the running period. The addition of the DRV concentrated the eluent in the reservoir via suppressed water removal after the detector (Fig. 4). This enabled the system to compensate for the addition of water by electrodialysis, loss of potassium on injection and dilution due to potassium leakage. The microcontroller was programmed to open, or activate the DRV by a ratio of time shown below

$$\text{DRV activation time (minutes active h}^{-1}) = 60\text{ min}\left(\frac{\text{Dilution rate (ml h}^{-1})}{\text{Pumped volume (ml h}^{-1})}\right) \qquad (3)$$

The activation of the DRV resulted in a stable eluent concentration (23 mM KOH), which was pumped at a rate of 0.5 mL min^{-1}.

In order to fully suppress the eluent in the ERD, it was necessary to determine the minimum current setting. The current setting was based upon the flow rate, eluent concentration and a suppression factor as shown in Eq. (4) [7,25]. The theoretical current efficiency for suppressing 23 mM KOH is 28.4 mA, using the standard suppressor factor of 2.47. This factor is based on the geometry, flow path and ion exchange surface area [25,26]. As stated previously, excess current was needed to ensure complete suppression. A standard increase of 20% was added to the suppression factor to account for the excess current needed, giving an adjusted factor of 3.0. Therefore, the ERD current was set to 34 mA (27 V). This was determined to be the minimal current for full eluent counterion suppression.

$$\text{ERD current setting (mA)} = \text{Flow rate (ml min}^{-1})\ \text{Eluent conc. (mN)}\ \text{Suppression factor} \qquad (4)$$

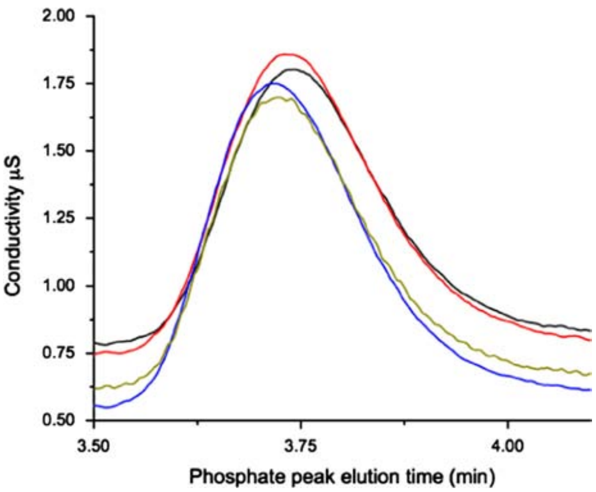

Fig. 6. Phosphate retention time through six eluent cycles with DRV. Column: 4 × 100 mm Dionex AS11, eluent: 23 mM KOH, flow rate: 0.50 mL min^{-1}, Injection volume: 20 µL, standard: 7.35 mg L^{-1} phosphate, red: cycle 1 + 150 nS cm^{-1}, black: cycle 5 + 100 nS cm^{-1}, green: cycle 8 + 50 nS cm^{-1}, blue: cycle 9. The dilution relief valve (DRV) was able to effectively remove water from the system and keep the KOH concentration relatively stable. The RSD of the phosphate peak elution time between the first and eighth cycles (48 h of operation) was equal to 0.21%.

An experiment was conducted to determine the effect of the DRV on phosphate peak reproducibility. The elution times of phosphate were recorded over eight eluent cycles (48 h of continuous operation) and are shown in Fig. 6. The addition of a DRV significantly stabilized the phosphate elution time (RSD = 0.21%) in relation to the system without a DRV (RSD of phosphate elution time = 3.7%), as shown in Figs. 5 and 6. These results indicate that the DRV could effectively maintain eluent concentration throughout operation of the system, providing reproducible peaks for phosphate.

The reliability of the ERD was determined by analyzing the stability of the chromatograms over time. Initially, 300 mL of 23 mM KOH eluent was prepared and pumped at a flow rate of 0.5 mL min^{-1}. The device was not operated in reflux mode for the first 120 ml to equilibrate the system. Once the system was stable, indicated by a steady voltage (27 V at 34 mA), reflux mode was enabled. In reflux mode, the baseline remained steady around 1.0 µS cm^{-1} with a total drift of less than 100 nS during 24 sequential, 1 h injections. Two subsequent 20 µL injections were made giving elution times for chloride, sulfate, and phosphate of 1.39, 1.83, and 3.69 min, respectively. After 24 h of continuous operation, two subsequent injections of the same standard gave elution times of 1.40, 1.84, and 3.70 min respectively. The chromatograms of the first and fifth cycle injections are shown in Fig. 7. The RSD of the elution time between the first and fifth cycle injections was calculated to be 0.21%. These preliminary results demonstrate the reliability of the ERD over five eluent cycles.

Due to the fact that there is a dilution of eluent in an ERD, the operating time of an ERD is limited based upon the volume of the eluent reservoir. Assuming that the rate of dilution remains constant throughout operation, it is possible to calculate the maximum operation time of an ERD, or amount of time until the eluent reservoir is depleted. In the system tested, a dilution rate of 1.34 mL h^{-1} was observed and the reservoir volume was initially 180 mL. Therefore, the system had a operating capacity of 134 h.

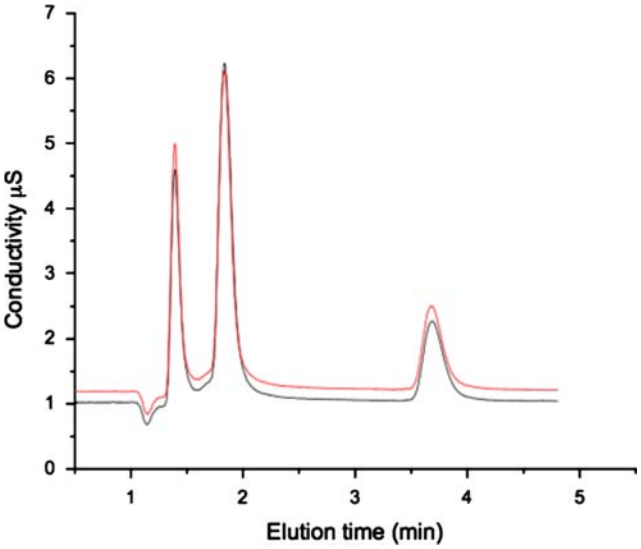

Fig. 7. Typical chromatographic performance. Column: 4 × 100 mm Dionex AS11, eluent: 23 mM KOH, flow rate: 0.50 mL min^{-1}, injection volume: 20 µL, standard: 2.45 mg L^{-1} chloride, 4.65 mg L^{-1} sulfate, 7.35 mg L^{-1} phosphate, red: cycle 1+50 nS cm^{-1}, black: cycle 5. The typical chromatographic performance after 24 h of operation is shown here. The DRV was used to maintain the eluent concentration. The RSD of the two injections during the first cycle compared to the two injections during the fifth cycle was equal to 0.21%.

One cycle was defined as the amount of time required to pump one complete reservoir volume. Since the system had a flow rate of 0.5 mL min^{-1}, one cycle was equal to 6 h. Thus, the system tested was capable of completing 22 cycles before the reservoir was depleted. If a longer operation time was required, the reservoir volume could be increased.

4.2. Eluent stratification

The switching of the DRV results in varying concentrations of KOH eluent returning to the eluent reservoir. An experiment was conducted to determine if the varying concentration of KOH eluent returning to the eluent reservoir would cause stratification of the reservoir. When the DRV is activated, fluid flow from the suppression chamber passes through the conductivity cell and is then directed to waste, instead of returning to the reflux chamber (Fig. 4). Nevertheless, ion electromigration continues to transport potassium to the reflux chamber from the suppression chamber, whether the DRV is activated or not, resulting in KOH accumulation. When the DRV is deactivated, fluid flow is redirected to reflux chamber, instead of waste, and sweeps away the KOH accumulating while the DRV was activated. A constantly agitated eluent reservoir was compared with an undisturbed reservoir for one full eluent cycle. There was no stratification observed in either eluent reservoirs, demonstrating that eluent stratification was not induced by DRV switching.

4.3. Eluent polishing

Eluent polishing is necessary in order to maintain a low background conductivity, especially when using prepared eluents. Without the electrolytic eluent polisher (EEP) after the pump, the background conductivity of the eluent was typically 2.0–3.0 µS cm^{-1} and had a relatively high drift (±1.0 µS over 24 h). With the electrolytic eluent polisher in place before the injection valve, the background conductivity was reduced to 1.0 µS cm^{-1} and had much lower drift (±0.1 µS over 24 h). Because of the relatively slow turnover of the eluent reservoir, atmospheric CO_2 is able to dissolve in the eluent as carbonate, causing higher background conductivities. Placing the EEP just prior to the injection valve ensured a stable and lower background. It is virtually impossible to completely eliminate carbonate from a hydroxide eluent, though it can be controlled, as is shown by the low drift with the EEP installed.

4.4. Sample pre-treatment

Samples also underwent pre-treatment to avoid the loss of suppressor capacity[13]. Before the injector, samples were pumped through a cation exchange bed in the hydronium form. This resulted in all sample cations being exchanged for hydronium, converting all analytes to their acid form. Without this treatment, polyvalent cations can permanently displace hydronium or potassium. Such a displacement could result in the permanent removal of resin capacity of the device. After the resin capacity is sufficiently depleted, the continuous operation of the device must be interrupted so that the resin beds can be regenerated.

4.5. Suppression limitations

As with all suppressors, concessions must be taken to maximize either suppression capacity or chromatographic efficiency. The combination of the bed volume and the resin capacity dictates the total suppression capacity. A small suppressor void volume has a high chromatographic efficiency, but has limited suppression capacity. Larger suppressor void volumes have higher suppression capacities, but cause peak broadening and reduce chromatographic efficiency. In the ERD, a suppressor void volume of 42 µL (4 × 10 mm) was chosen to give relatively good chromatographic efficiency, while also being able to suppress up to 25 mM KOH. This was the minimum functional size the suppressor could be while still fully suppressing 20–25 mM KOH eluent at a flow rate of 0.5 mL min^{-1}.

5. Conclusions

In summary, this work has demonstrated that electrodialytic, multi-chambered devices can be effectively used for isocratic eluent generation and suppression, while conserving nearly all of the eluent. When applied to IC, eluent reflux provides a system that operates autonomously, while delivering stable chromatographic performance. The real advantage of eluent reflux is having the robustness of a conventional IC system, which is limited only by the eluent dilution rate. Though there is a potential for retention times to increase during reflux mode due to dilution; however, this was negated by the addition of the DRV, which served to counterbalance dilution. By using the DRV, the device retains full suppression and separating capabilities, while also maintaining a very stable eluent concentration. Running several eluent cycles through the ERD demonstrated the reliability of the device, while recording stable phosphate elution times showed reproducibility.

While the principles of eluent reflux have been shown in this work, further work is necessary in order to improve the functionality of the ERD. Since it now appears that the dilution rate is the greatest limitation of the ERD, it is suggested that further research be conducted on methods for reducing the rate of dilution.

As more field applications become available for IC, it is anticipated that compact units like this will be an increasingly popular consideration for analyses. Typically, the best field instruments have low power consumption, are robust in design and can operate almost autonomously. Therefore, eluent reflux meets the criteria for a potential field employable technique. There is also a cost-benefit associated with the prospect of direct field measurements. Sampling could be automated and measured in real time, giving greater resolution and less handling error. Though this unit has only been tested for anions, analogous devices could be easily adapted for cations. It is believed that there is a unique advantage to this application, especially in field-based instrumentation in the realm of environmental sciences.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.11.019.

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