



Improvements in ion reflux: An electrodynamic eluent generation and suppression device for ion chromatography



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ABSTRACT

This work describes a membrane based electrodynamic ion reflux device (IRD), which uses water as the pumped phase and integrates isocratic and gradient eluent generation and suppression. The current design incorporates several ion exchange membranes to create discrete chambers for suppression and eluent generation, while isolating the electrodes from the analytical stream. A small volume of recycled water can be used as the pumped phase while continuously refluxing the eluent ions. This current design permits electronically controlled eluent generation of at least $16.4 \mu\text{eq KOH min}^{-1}$, while maintaining low suppressed background conductivity ($<0.5 \mu\text{S/cm}$). The device was operated in gradient or isocratic mode continuously for up to 6 weeks. During this period, over 500 gradient and isocratic injections were performed, showing peak retention time precision below 1.5% RSD.

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1. Introduction

The introduction of electrodynamic ion exchange devices has revolutionized ion chromatography (IC) [1–4]. The ability to electrolytically control the generation and suppression of eluent in ion chromatography, has eliminated the most common operator variable, eluent preparation, and has led to more precise, reliable and simplified analyses [5]. State-of-the-art IC systems have electrodynamic capabilities for eluent generation and suppression, but there is still a consumption of eluent stock that eventually must be replenished [6,7]. In addition, water, which is the reagent of largest volume used in IC, must be regularly replenished and the variation in water quality can have a significant impact on the purity of the electrolytically generated eluent. The current practice of IC requires an equilibration period, making continuous operation of the system desirable. However, this results in the continuous consumption of water and eluent stock, as well as the production of chromatographic waste. Furthermore, replenishing the eluent stock can come at a considerable cost to the user.

Ion reflux was the first technique to integrate electrolytic eluent generation and suppression using water as the pumped phase to preserve the source of the eluent co-ion [8–11]. By integrating two intimately linked processes, the consumed eluent could

be passed back to the eluent generator portion of the device for reuse, rather than being directed to waste. This created a “reservoir” for the eluent counter-ions, which refluxed between the suppression and eluent generation regions. One limitation of IRD-1 and IRD-2 [8] however, was that the pumped phase was exposed to the electrodes resulting in the introduction of electrolysis gases. These gases had to be dealt with downstream by adding a flow restrictor at the conductivity cell outlet for detection [8]. Commercial eluent generators also expose the eluent (analytical) stream to an electrode and the consequences of the formation of gas and electrochemical by-products must be dealt with [10–15].

A means of reducing electrolysis gases and electrochemical by-products from the eluent requires isolating the electrode chambers from the eluent stream using ion exchange barriers or membranes [5,16]. One example of this is an eluent reflux device (ERD) as seen in Fig. 1. An ERD uses multiple membrane-separated chambers to isolate the electrodes from the eluent stream and is able to reflux isocratic eluents [17]. Using the ERD, a bottle of manually prepared eluent is suppressed, recovered and returned back to the eluent bottle, essentially free of electrolysis gases and electrochemical by-products.

In this paper, we describe a third kind of ion reflux device (IRD-3), which operates in the same way as an ERD [16], only using water, not prepared eluent as the pumped phase (Fig. 1). Because the pumped phase in ion reflux is water and not eluent, ion reflux also allows the user to perform gradient analysis. The IRD-3 operates in the same manner as the first IRDs, while isolating the electrodes

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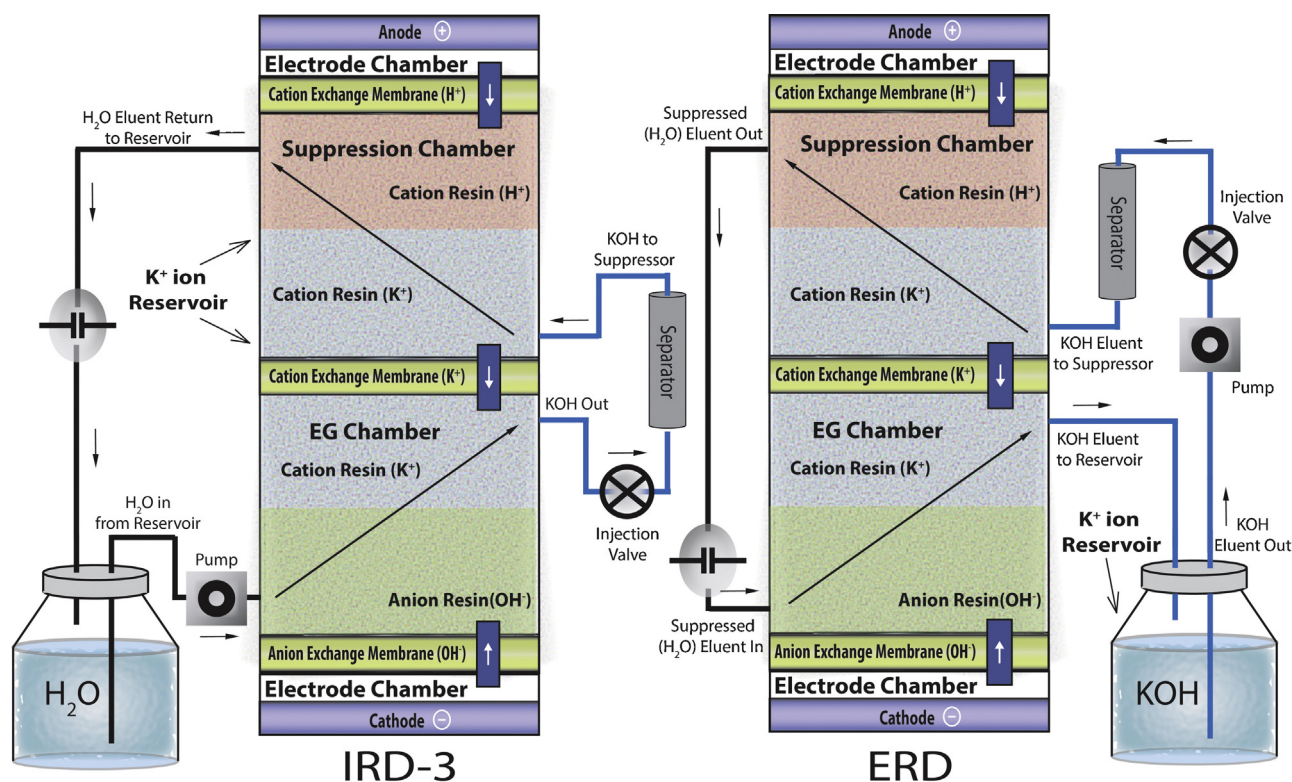


Fig. 1. Schematic of an IRD-3 versus an eluent reflux device (ERD). The reservoir of potassium in the IRD-3 is located in the portion of the suppressor bed in the potassium form, whereas it is the eluent bottle in the ERD. The ERD is only capable of suppressing and regenerating the isocratic eluent, which can be returned to the eluent bottle while the IRD-3 can generate and suppress varying eluent concentrations. Blue tubing indicates KOH flow, whereas black tubing indicates water or suppressed eluent flow. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

from the eluent stream. While the same IRD-3 concept can be applied for cation analysis (with acid eluents), this paper focuses on the IRD-3 for anion in analysis with potassium hydroxide as the eluent.

2. Principles

2.1. Electrodialysis

Potassium hydroxide eluents can be generated using a reservoir containing concentrated KOH and an anode with a cation exchange membrane or barrier, which separates a liquid channel containing the cathode, commonly referred to as an eluent generator [2,3]. As seen in Fig. 2, when water is pumped through the eluent generation (EG) chamber and an electric field is applied, potassium ions move from the KOH reservoir, across a K^+ form cation exchange membrane where the potassium ions combine with the reductive electrolysis product, hydroxide, to form potassium hydroxide (KOH). This same principle applies in ion reflux. In IRD-3 however, a separate water source (orange tubing in Fig. 3) is directed to the electrode chambers to serve as the source of hydronium and hydroxide for suppression and eluent generation, respectively. The cation exchange membrane, which is positioned near the suppression chamber outlet, is adjacent to the anode (H^+ form cation exchange membrane in Fig. 2). At the anode, hydronium ions are produced, and under the force of the electric field, migrate through the cation exchange membrane toward the cathode. This is the source of regenerant (hydronium ions), which contributes to the Hydronium-Potassium, or H-K boundary created in the suppression chamber, as seen in Fig. 2. Oxygen gas and oxidative electrochemical by-products generated at the anode are prevented from entering the suppressed eluent by the cation exchange membrane. At the cathode, hydroxide ions are produced, and under the force of the

electric field, migrate through the anion exchange membrane (OH^- form membrane in Fig. 2) toward the anode. This is the source of eluting ions (hydroxide), which combine with migrating potassium ions from the suppression chamber to form the KOH eluent. Hydrogen gas and reductive electrochemical by-products produced at the cathode are prevented from entering the newly generated (refluxed) eluent by the anion exchange membrane. The influx of ions into the resin beds causes a net movement of hydronium and hydroxide toward the K^+ form cation exchange membrane, as seen in Fig. 2.

In the suppression chamber, incoming K^+ exchanges with hydronium ions (from the anode) migrating toward the cathode, where suppression occurs. This effect of hydronium ion migration opposite to KOH flow creates the H-K boundary in the suppressor resin bed, as seen in Fig. 2. The portion of K^+ form resin in the resin bed serves as the K^+ ion reservoir for the generation of KOH, shown in Figs. 1 and 2. For each hydronium that enters the device, one K^+ ion is displaced toward the EG chamber eventually making its way to the potassium hydroxide, or K-OH formation boundary in the EG chamber. Because electrolysis is stoichiometric, each hydronium ion that enters the resin bed from the anode is accompanied by the entry of a hydroxide ion from the cathode. When an electric potential is applied, hydroxide ions entering at the cathode end of the EG chamber propagate through anion exchange resin bed. In doing so, they displace other hydroxide ions until they reach the K-OH boundary where KOH is formed. Under constant flow and a stable applied current, a precise concentration of KOH is produced.

2.2. Ideal faradaic behavior

In any device containing both anion and cation exchange materials deviations from ideal or unity faradaic behavior (i_{eff}) are seen as a result of water splitting at the interface between the anion

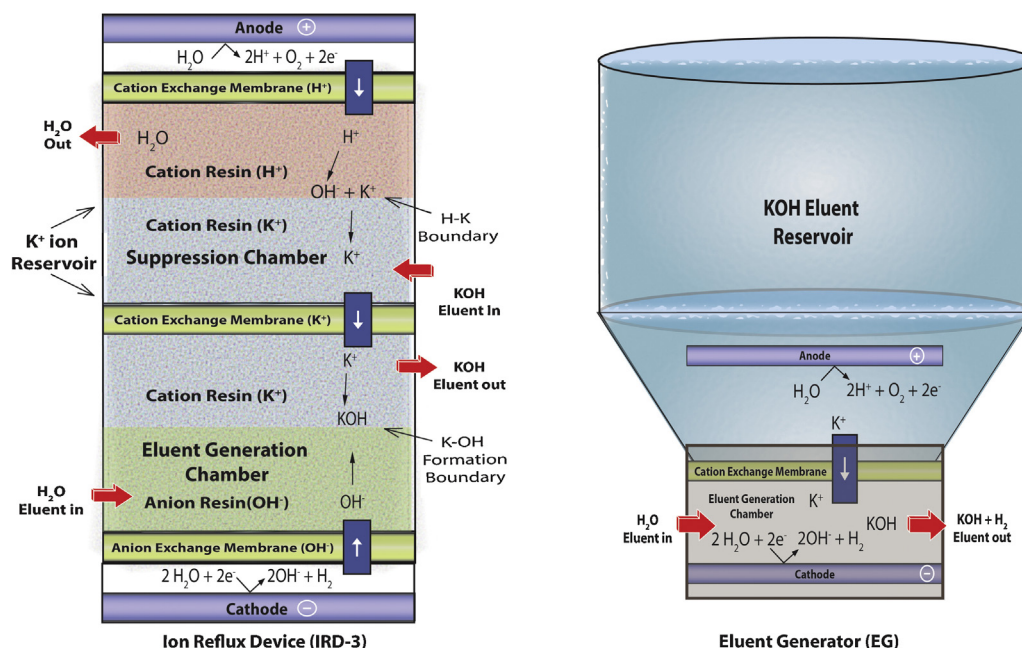


Fig. 2. Schematic of an IRD-3 versus an eluent generator. The red arrows show liquid flow through the various chambers. White arrows indicate ion transport across an ion exchange membrane. The H-K boundary is where incoming KOH is suppressed to water, and the K-OH formation boundary is where hydroxide ions meet potassium ions to form KOH eluent. Electrode half reactions are shown in their respective electrode chambers. Also noted is the source, or reservoir of potassium ions for the given device. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

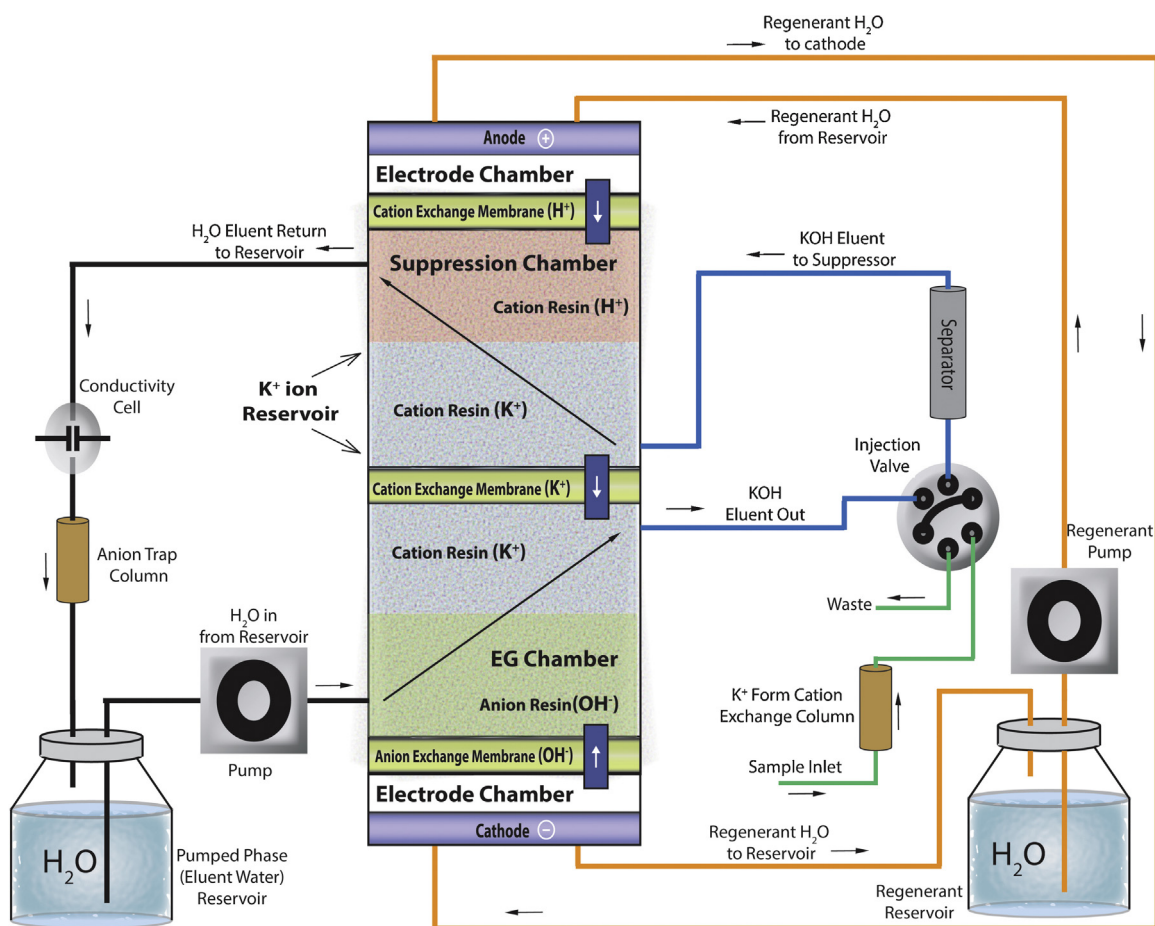


Fig. 3. System schematic of an IRD-3 and accompanying components. The black line represents water flow, blue represents KOH flow, green represents sample flow and orange represents regenerant water flow. The black arrows show the relative direction of flow throughout the schematic. The only regenerant water that comes into contact with the analytical stream is the water which accompanies hydronium and hydroxide transport across the ion exchange membranes at the electrodes. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

and cation exchange materials [16]. Under ideal conditions where water splitting does not occur, 0.625 mmol of KOH/mA can be produced. Furthermore, the applied current combined with the flow rate can be used to calculate the theoretical concentration of the eluent [3]. Samples were generated by the IRD-3 and subsequently analyzed for potassium by ICP-OES. The i_{eff} for the IRD-3 was calculated by dividing this measured concentration by the theoretical concentration, shown in Fig. S1.

Supplementary Fig. S1 related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma.2015.05.027>

2.3. Donnan leakage

In addition to non-faradaic behavior, loss of potassium through Donnan leakage can be detrimental to ion reflux. As seen in Fig. 1, the green portion of the eluent generation chamber is packed with anion exchange resin in the hydroxide form to prevent the locally high concentration of KOH produced at the K-OH formation boundary from being lost through the anion membrane [18]. In addition to minimizing the potential for KOH loss to the cathode compartment, the hydroxide-form resin layer ensures uniform, laminar flow across the K-OH formation boundary.

3. Experimental

3.1. Fabrication of the IRD-3

To ensure proper operation of the device under a backpressure of 1500 psi, a compression design was implemented. Once assembled, 4 PEEK sections housed 2 electrode chambers, and the suppression and EG chambers, as seen in Fig. 3. At each end of the device, an electrode chamber housed the Pt-mesh electrodes and contained ports for the electrical lead, regenerant water inlet and outlet. Inlet and outlet ports were also machined into the PEEK sections containing the resin beds to direct flow across the EG and suppression chambers. A representation of fluid flow across the IRD-3 is depicted using black arrows in Fig. 3.

The resin bed ports were designed in a manner that each would enter their respective resin beds at the membrane-resin interface. The device was plumbed so that water (black tubing) entered the EG chamber at the cathode end, flowed toward the anode end and exited as KOH (blue tubing), as seen in Fig. 3. After separations, the KOH (blue tubing) flowed to the suppression chamber at the cathode end as seen in Fig. 3. Flow was directed toward, and exited the suppression chamber near the anode as water (including anionic analytes). After detection, the suppressed eluent (black tubing) could be either stripped of anions and returned to a water reservoir for reuse as seen in Fig. 3, or directed to waste (not shown).

The suppression chamber (4 mm id \times 10 mm long) was separated from the anode electrode by placing a stack of three I-100 hydrogen form cation exchange membranes (Snowpure LLC, San Clemente, CA) at the suppressor outlet. The suppression chamber was then filled about one-third with Dowex 50Wx4 100–200 mesh hydrogen form strong acid cation exchange resin (Sigma–Aldrich Co., St. Louis, MO), at approximately 45% moisture content. The remaining two-thirds of the bed was filled with the same resin in the potassium form. The interface of the two resin forms created the (H-K) boundary, as seen in Fig. 4. Incoming KOH flowed toward the H-K boundary where it was suppressed by hydronium migrating in the opposite direction of flow resulting in the formation of water. The potassium form portion of the resin bed served as the potassium reservoir (Fig. 3), and was used for KOH eluent formation in the EG chamber. At the suppressor inlet, a stack of three I-100 potassium form cation exchange membrane (Snowpure LLC,

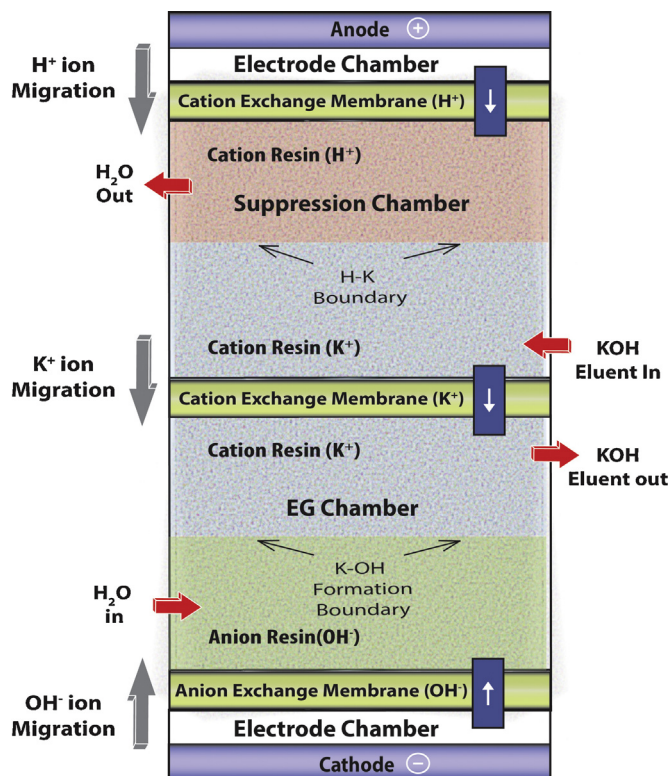


Fig. 4. Diagram of an IRD-3 showing the general direction of ion exchange membrane transport (white arrows), ion migration potential (gray arrows) and bulk fluid flow in and out of the chambers (red arrows). (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

San Clemente, CA) was placed to serve as a fluid flow boundary between the suppression and EG chambers.

Likewise, the EG chamber was separated from the cathode by a stack of three I-200 hydroxide form anion exchange membranes (Snowpure LLC, San Clemente, CA) at the EG inlet. This was done to separate the cathode electrode from the EG chamber. The 4 \times 10 mm chamber was then filled about one-half with Dowex 1x4 100–200 mesh hydroxide form strong base anion exchange resin (Sigma–Aldrich Co., St. Louis, MO) at 45% moisture content. The remaining half of the resin bed was filled with the same potassium form cation exchange resin used in the suppressor. The interface of the hydroxide and potassium form resins served as the region of KOH generation used for chromatographic elutions. The four components were then stacked and bolted together to form a multi compartment, electrically conducting device. By doing this, liquid flow boundaries were created by the membranes, while ions could move freely through their respective membranes. This created the mechanism for which potassium ions could be refluxed across the K⁺ form cation exchange membrane, as seen in Fig. 4.

Once assembled, the IRD-3 was pumped with water using a GP40 chromatography pump (Dionex Corp., Sunnyvale, CA) at 0.25 ml/min to fully hydrate the resin beds. As the resin and membranes became fully hydrated, good electrical contact between the resin and membranes was achieved. A low drift, constant current power supply built in-house, powered the IRD-3. The current supplied to the device ranged from 0.22 to 28.5 mA at 0.18 mA increments with an accuracy of ± 2 μ A. The applied voltages ranged from 0 to a maximum of 21 V. The power supply also contained an on/off function, which allowed the supplied current to be completely disabled (0 μ A).

After the baseline conductivity was stable, the IRD-3 was plumbed into a chromatography system containing a CD20 conductivity detector, 2 \times 50 mm, 9 μ m diameter microporous resin AG-15

guard column (Dionex Corp., Sunnyvale, CA), and 6-port, high-pressure injection valve (VICI Valco Instruments Co. Inc., Houston, TX) with a 20 μ l injection loop, as depicted in Fig. 3. No temperature stabilization system was used throughout the experiments and all reported results were at room temperature ($22 \pm 2^\circ\text{C}$). Chromeleon 6.8 software (Dionex Corp., Sunnyvale, CA) was used to collect and analyze the data. A current of 9.14 mA (9.6 V) was applied to the IRD-3 and left to stabilize for several hours. At 0.25 ml/min and an applied current of 9.14 mA, the KOH eluent produced was approximately 21 mM.

It was determined by the suppressed baseline conductivity (drift), that this current was sufficient to maintain a stable background and remove any residual carbonate from the anion exchange material in the EG chamber and guard column.

All reagents used were ACS grade. The procedures for membrane and resin conversions are discussed in greater detail in [16].

4. Results and discussion

The reproducibility of the chromatography and the faradaic behavior as a function of the applied current were two major parameters investigated in the evaluation of the IRD-3. Various embodiments of the IRD-3 were built and tested during the course of this work. The data presented in this paper is from an IRD-3 device that has operated continuously for over six weeks.

4.1. Chromatographic reproducibility

The first test of the IRD-3 was under isocratic conditions where the applied current was 14.0 mA (12.7 V) and the flow rate was 0.25 ml/min (corresponding to approximately 32 mM KOH). Fig. 5 shows an example chromatogram of an isocratic elution. Over an 8-h period a standard solution was injected approximately every 30 min Table 1 shows the %RSD and average retention times of 10 injections during the 8-h period. The current applied to the IRD-3 was held constant for the duration of the analysis period, including loop loading. While the %RSD and retention times in the chromatography are affected by the fluctuation ($\pm 1^\circ\text{C}$) in ambient air temperature, this has a negligible effect on the performance of the IRD-3.

One of the advantages of ion reflux is the ability to perform gradient elutions. Gradient elutions were performed using the same IRD-3 and AG15 column used for the isocratic separations. In order to ensure reproducible conditions for gradient analysis, a 2.5-min equilibration period was placed at the beginning of each run. This was done to standardize the time between the standby eluent concentration of 46 mM KOH and the starting concentration of the gradient of 15 mM KOH. During gradient analysis, the flow rate was 0.25 ml/min and the gradient program was 15–21 mM from 2.5 to 5.5 min, and 21–46 mM KOH from 5.5 to 12 min, with a total run time of 20 min (including the 2.5-min equilibration). Over an 8-h period a standard solution was injected approximately every 30 min Table 2 shows the %RSD and average retention times of 10 injections during the 8-h period. The variation seen in the %RSD and retention times in the chromatography is mainly a contribution

Table 1
Isocratic 10 runs in 1 day no temperature control.

Analyte	Retention time (min)	%RSD
Fluoride	0.86	0.46
Chloride	1.68	1.01
Nitrite	2.14	1.06
Sulfate	3.00	1.43
Bromide	4.35	0.56
Nitrate	5.05	0.63
Phosphate	8.62	0.74

Table 2
Gradient 10 runs in 1 day no temperature control.

Analyte	Retention time (min)	%RSD
Fluoride	1.22	0.57
Chloride	3.25	0.59
Nitrite	4.16	0.82
Bromide	7.85	1.16
Nitrate	9.02	1.18
Sulfate	8.82	1.18
Phosphate	15.19	0.81

of the fluctuation ($\pm 1^\circ\text{C}$) in ambient air temperature. The current applied to the IRD-3 during loop loading and injection was the same (35 mM KOH) for each injection throughout the duration of the analysis period, including loop loading. In both, the isocratic and gradient operating modes, the IRD-3 exhibited an average retention time stability of 0.87% RSD.

The performance of the IRD-3 was also compared to the performance data of the IRD-1 and IRD-2 in the literature. It was found that the IRD-3 in fact, exceeded the performance of its predecessors [8–11]. Furthermore, the 0.87% RSD for the IRD-3 exceeds the EPA requirement of 2% for samples of the same nature over a similar analysis period [19].

4.2. Faradaic behavior

In addition to the stability of the eluent concentration, it was also demonstrated that the faradaic behavior of the device was linear over the range of current applied (0.22–28.5 mA), shown in Fig. S2. Furthermore, based on the slope of the plot in Fig. S1, it was concluded that the electrochemical conversion efficiency over the range of currents applied was stable. During the 6 weeks of constant operation, there was no change in the concentration of the KOH produced by the IRD-3 as indicated by the conductivity of the eluent generator outlet.

Supplementary Fig. S2 related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chroma.2015.05.027>

While the main difference between the IRD-3 and the earlier IRDs was the addition of anion exchange material at the cathode, this alone cannot explain the non-ideal faradaic behavior seen [3,5,8]. The source of the non-ideal faradaic behavior, while most likely a cause of several factors including joule heating, faradaic impedance and water splitting, remains unclear and will require further examination [20–24].

4.3. Suppression capacity

In all suppressors, a compromise must be made to maximize either chromatographic efficiency or suppression capacity. In the IRD-3 at a flow rate of 0.25 ml/min and 28 mA applied current, the measured IRD-3 eluent concentration was 65 mM KOH, which corresponds to 16.4 $\mu\text{eq}/\text{min}$. While the device was able to operate and suppress eluents up to 16.4 $\mu\text{eq}/\text{min}$, extensive joule heating caused by 28 mA of current being passed through the 4 mm diameter membrane caused significant burning of the cathode membrane. Therefore, it was concluded that the device should not be operated at currents higher than 20 mA, which corresponds to a maximum eluent concentration of 50 mM KOH at 0.25 ml/min. Throughout the operation of the device, no loss of KOH at the suppressor outlet was detected. During routine operation of the IRD-3, a Trovion CIRA10 electrolytic water polisher (Trovion Company, Campbell, CA) was used at the pump inlet, to remove trace ionic contamination and carbonate from the feed water (pumped phase), which, resulted in background conductivities of 150–500 nS/cm. While the IRD-3 was not extensively tested at other flow rates, a previous study done using a similar device [16] showed that a

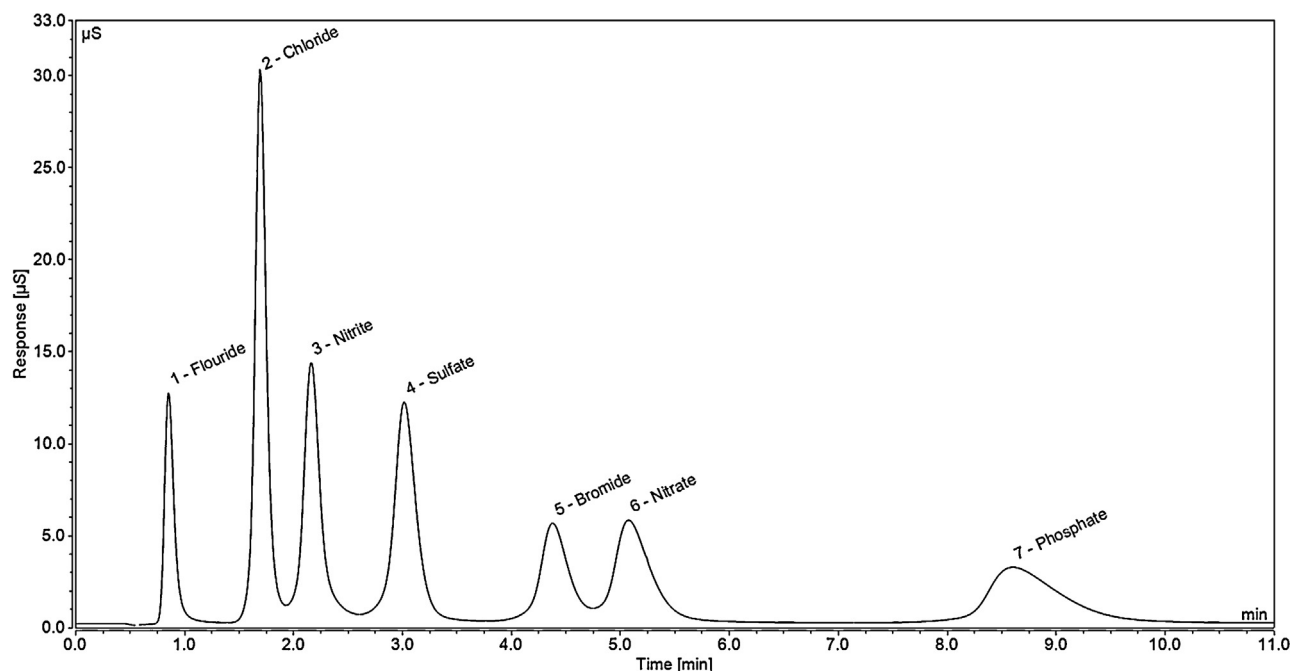


Fig. 5. Chromatogram of an isocratic elution. Column: 2×50 mm AG15. Flow rate 0.25 ml/min. Injection volume: 20 μ l. Eluent type: KOH. Eluent concentration: 32.4 mM. Relative temperature 22 $^{\circ}$ C (no temperature control). Analyte concentrations injected: 1.0 ppm F^{-} , 1.5 ppm Cl^{-} , 5.0 ppm NO_2^{-} , 5.0 ppm NO_3^{-} , 5.0 ppm Br^{-} , 7.5 ppm SO_4^{2-} , 7.5 ppm PO_4^{3-} .

maximum of 13.5 μ eq/min could be suppressed at 0.5 ml/min. This suggests that the slower flow rate and therefore longer residence time of potassium in the suppression chamber may have a role in suppression capacity.

4.4. Eluent reservoir capacity

In addition to the suppression capacity, the suppressor volume and the portion of the suppression chamber resin bed in the potassium form also determines the capacity of the eluent reservoir. The continuous operation of the device relies on the H-K boundary in the suppressor because the portion of the suppressor in the K^{+} form serves as the potassium reservoir for eluent production, as seen in Fig. 3. When the device is first polarized the H-K boundary moves toward the K^{+} form cation exchange membrane. Table 3 shows the extent of the potassium reservoir that is consumed during polarization of the IRD-3 depicted in Fig. 3. When the IRD-3 is first polarized, K^{+} ions begin to flux from the suppressor bed into the eluent generation chamber. This process continues until returning KOH at the suppressor inlet can replenish the potassium reservoir in the suppression chamber. However, if hydronium ions from the anode flux beyond the suppression chamber inlet, hydronium, rather than potassium ions can be fluxed into the EG chamber. When this occurs a portion of the applied current is used to form water rather than

eluent and the linear relationship between applied current and eluent concentration breaks down [8,9].

In order to conserve the eluent ion reservoir of the IRD-3, the approach of lowering or turning off the current (thereby reducing eluent concentration) prior to switching the injection valve from the inject to load position (in the inject position, the sample loop has eluent flowing) was investigated. This was done after each chromatographic run allowing the KOH (blue tubing in Fig. 3) to return to the potassium reservoir in the suppressor. In addition to collecting the KOH, the sample injection loop was flushed of KOH so that only a loop volume of water (not eluent) would be lost during sample loading.

At 0.25 ml/min flow rate, the KOH concentration was about 0.18 mM after 90–100 s of operation with zero applied current. Based on the construction described in Section 3.1, approximately 2/3 of the resin volume in the suppression chamber was in the potassium form. Assuming about 110 μ eq of potassium to be present in the eluent reservoir, the predicted maximum number of injections was calculated before hydronium breakthrough occurred [18,25,26]. These values are listed in Table 3. The resulting chromatography using this method was identical to the results in Tables 1 and 2, with the only difference being an increase in analysis time due to the zeroing of the current.

In addition to turning the current off prior to switching the injection valve to the load position, the potassium reservoir could also be replenished by injecting a sample loop volume of concentrated KOH stock intermittently. Using this method, 20 μ L of a 1.7 M KOH stock solution was injected into the system at a rate equivalent to the removal of potassium. For example, after 50 isocratic injections at 34 mM KOH, a sample loop volume of 1.7 M KOH was injected. The 34 μ eq of potassium injected was equivalent to the number of μ eq of potassium removed during the 50 previous injections where 20 μ L of 34 mM KOH was lost to waste. During each injection, the necessary number μ eq of K^{+} ions could be added to the reservoir stock depending on the concentrate injected. This injection regime could be done daily, or in conjunction with system calibration, shut-down or standby operation. The resulting chromatography from

Table 3
H-K boundary movement under different applied currents.

μ mol K^{+}	K^{+} conc. (mM)	%H-K boundary shift	Injections
0.78	10.62	0.70	142
1.36	18.68	1.23	81
1.79	24.57	1.62	61
2.25	30.76	2.03	49
3.12	42.73	2.82	35
3.71	50.78	3.35	29

Injections are assuming water is used. Potassium reservoir starting at 110 μ eq. μ mol of K^{+} determined by the concentration in mM multiplied by the dead volume of the system (73 μ L).

this method to recharge the reservoir was also compared to the chromatography from Tables 1 and 2, and showed no significant difference.

4.5. Sample injection volume and pre-treatment

Because of the limited size and capacity of the suppression chamber, the effects of analyte co-ions on the cation exchange resin were also considered. As discussed previously [16], polyvalent cations can displace weaker bound ions, permanently removing ion exchange capacity. To prohibit this from happening, a cation exchange column in the potassium form was placed at the injection valve sample inlet (green tubing), as seen in Fig. 3, to exchange polyvalent sample cations to potassium. This maintained the suppressor bed ion exchange capacity of the IRD-3.

5. Conclusions

This work has demonstrated the feasibility of a new embodiment of ion reflux with all the advantageous of the early ion reflux concept, but with the added advantages of no gas production in the analytical stream and the ability to recycle the water used to electrolytically generate eluent. This results in a chromatographic system with virtually no significant waste production. The ability to change the current during the chromatographic analysis and maintain a linear and reproducible relationship between the applied current and eluent concentration makes IRD-3 compatible with gradient elution. We have shown that IRD-3 is capable of continuously recycling a small volume of eluent water, reducing the need for frequent filling of the water reservoir and minimizing waste disposal. Because both, the eluent ions and the water are recycled in IRD-3, the system can be left on without the concern of reagent consumption or waste generation.

IRD-3 was operated continuously for 6 weeks without a measurable change in its electrical or chromatographic behavior. While the principles of the IRD-3 have been demonstrated in this work, further work is planned to characterize the faradaic behavior of the device and to also demonstrate IRD-3 for cation analysis. As more applications become available for IC, it is conceivable that compact units such as this will be of increasing importance. For this reason, we see several opportunities where the principles of IRD-3 could be applied.

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