



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



Kyle Elkin<sup>a,\*</sup>, John Riviello<sup>b</sup>, Hamish Small<sup>c</sup>

<sup>a</sup> Norwegian University of Life Sciences, N-1432 Ås, Norway

<sup>b</sup> Trovion Company, Campbell, CA 95008, United States

<sup>c</sup> HSR, Ashland, OR 97520, United States

## ARTICLE INFO

### Article history:

Received 17 November 2014

Received in revised form 11 May 2015

Accepted 13 May 2015

Available online 22 May 2015

### Keywords:

Ion chromatography

Electrodialytic eluent generation

Ion reflux

## ABSTRACT

This work describes a membrane based electrodialytic 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.

Published by Elsevier B.V.

## 1. Introduction

The introduction of electrodialytic 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 electrodialytic 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

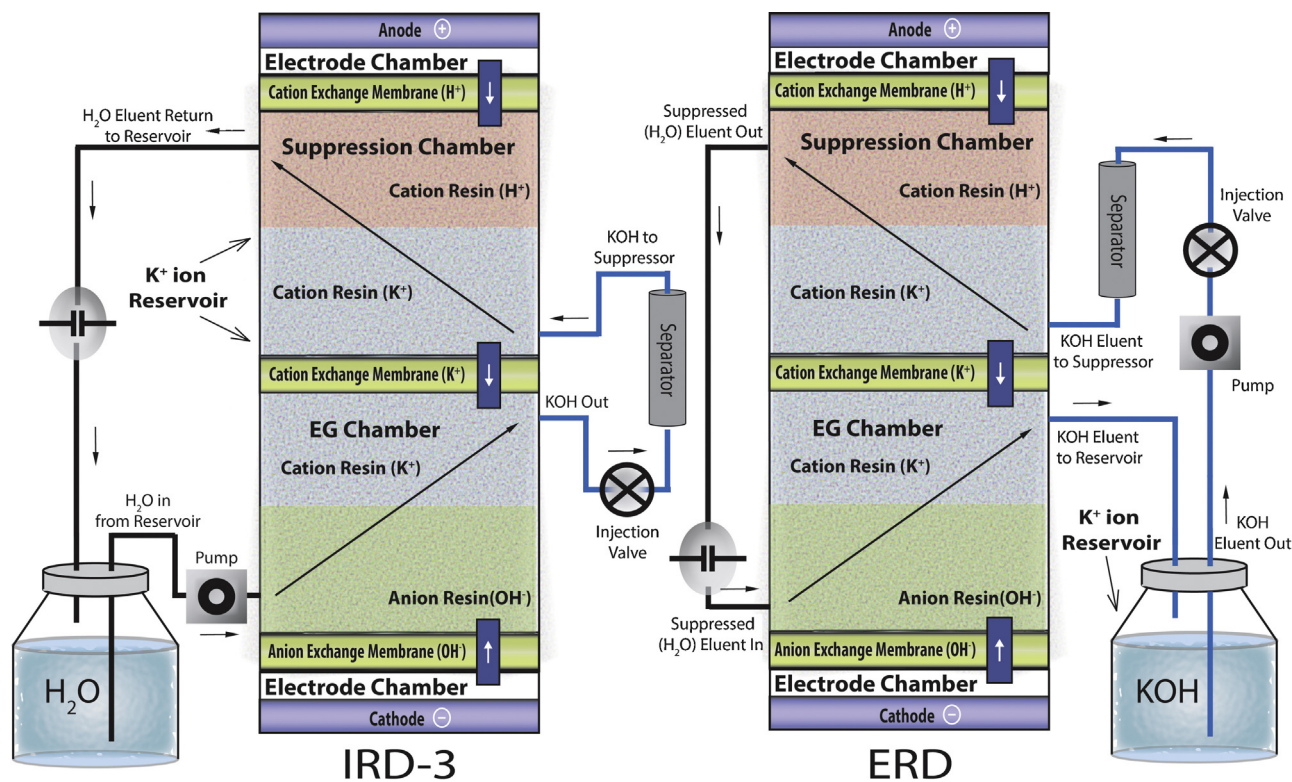
be passed back to the eluent generator portion of the device for reuse, rather than being directed to waste. This created a “reservoir” for the eluent counter-ions, which refluxed between the suppression and eluent generation regions. One limitation of IRD-1 and IRD-2 [8] however, was that the pumped 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

\* Corresponding author. Tel.: +1 814 865 9879.

E-mail address: [Kyle.elkin@ars.usda.gov](mailto:Kyle.elkin@ars.usda.gov) (K. Elkin).



**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 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<sup>+</sup> form cation exchange membrane where 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<sup>+</sup> 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<sup>-</sup> 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<sup>+</sup> form cation exchange membrane, as seen in Fig. 2.

In the suppression chamber, incoming K<sup>+</sup> 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<sup>+</sup> form resin in the resin bed serves as the K<sup>+</sup> ion reservoir for the generation of KOH, shown in Figs. 1 and 2. For each hydronium that enters the device, one K<sup>+</sup> 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

Download English Version:

<https://daneshyari.com/en/article/1201328>

Download Persian Version:

<https://daneshyari.com/article/1201328>

[Daneshyari.com](https://daneshyari.com)