Water, electricity and ion exchange; how Hamish Small sustained the evolution of ion chromatography

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ABSTRACT

Since the development of synthetic ion exchange resins in 1935, the electrochemical properties of these unique materials have intrigued researchers. In 1951, Hamish Small was introduced to synthetic ion exchange resin when he studied the electromigration of cations in these new materials. In 1955, he began working in the ion exchange division of the Physical Research Laboratory at Dow Chemical. In 1975, Small and co-workers described a new analytical tool, ion chromatography, which would revolutionize ion analysis. Twenty years after the commercial introduction of ion chromatography, Small demonstrated how an electrically polarized ion exchange resin bed could be used to produce an acid or base eluent using water as the pumped phase. Today, Small's inventions remain the core technology in state-of-the-art ion chromatography systems for electrolytic eluent production, purification, and suppression. This is a personal account of my collaboration with Hamish and how he sustained the evolution of ion chromatography for more than 50 years.

1. Introduction

Hamish Small is best known to the analytical chemistry community as the primary inventor of ion chromatography (IC) [1]. The early pioneering work which led to the development of IC at Dow Chemical in Midland, Michigan is well documented in several interesting manuscripts written by Small [2, 3]. As Hamish described, the invention of ion chromatography at Dow did not result from a formal project or corporate mandate. The motivation for its development arose from the necessity for a convenient technique to measure a variety of inorganic ions which exhibited diverse properties. The idea of a chromatographic technique to quantitatively measure a variety of ions in a single analysis was only a dream. In Hamish's own words “a few of us in the Physical Research Lab began to imagine the benefits of replacing these many wet chemical methods with a single chromatographic method that would be universally applicable to all ionic species.” So, while the origins of ion chromatography had rather subdued beginnings, the eventual invention and commercialization of the technology is one of the great analytical chemistry success stories of the 20th century.

2. Hamish and Dionex, the early days of suppression

In the fall of 1975, after IC had been licensed from Dow Chemical, the newly formed Dionex Corporation introduced the first commercial ion chromatography system. Hamish was still employed at Dow until 1983, and when he retired, he began consulting for Dionex. He worked out of his “basement” laboratory in Leland, Michigan and later that year would visit Dionex in Sunnyvale, California. I met Hamish for the first time during that visit to Dionex. I was working as a research chemist in the Dionex research and development group which was being led by Chris Pohl. The group was small, but focused, and there was a lot of fertile research ground to cultivate. It was an exciting time, as IC was all the buzz in the analytical community, Dionex was having success in commercialization of this new technology and the inventor of IC was now a consultant. Hamish and I remained in regular contact and during his subsequent visits, I made sure to show him the capabilities of the wineries and Italian restaurants in the greater San Francisco Bay area.

Suppressors, a key component in the development and invention of ion chromatography [4], were an active topic of research in the early days at Dow, Dionex and other groups. By the mid 1980’s, the original commercial, resin-based suppressor (packed bed suppressor or PBS) had been largely replaced with continuously, chemically regenerated membrane-based suppressors based on tubular (fiber suppressors) or planar (micromembrane suppressors) [5,6]. Chemically regenerated planar (flat) membrane suppressors offered high suppression capacity and low dispersion and were important components in the development of gradient separations in IC. Higher suppression capacity translated into higher regenerant flow rates, which proved problematic with respect to
the volume and disposal of the chemical regenerant. While continuously regenerated membrane-based suppressor brought new capabilities to IC, Hamish had some ideas on how PBS could be improved.

Hamish proposed the concept of using a small (low volume) PBS with frequent chemical regeneration, perhaps after every analysis. This contrasted with the teachings of the conventional PBS which were designed to operate for extended periods (4–8 h) before chemical regeneration was required. Hamish and I began working on this concept and we were able to demonstrate practicality of this idea for both isocratic and gradient ion chromatography. In 1993 a patent application was filed and in 1995 a US patent covering this invention was issued [11]. While this was never commercialized by Dionex, it was the subject of considerable commercial interest and eventually was licensed to Metrohm AG, Lachat Instruments Inc. also commercialized a suppressor based on the “small” chemically regenerated packed bed suppressor [12]. Meanwhile, Hamish had been rummaging through his “mental attic” and what would play out over the next several years would result in major advancements in IC technology.

3. Electrifying ion exchange resins

Early research on the electrochemical regeneration of ion exchangers using the electrolysis of water was applied to IC in the 1980’s in the form of electrodialytic suppressors. Early research on the electrochemical regeneration of ion exchangers using the electrolysis of water was applied to IC in the 1980’s in the form of electrodialytic suppressors [7–9]. Dionex introduced the first commercial electrodialytic membrane suppressor in 1992. Meanwhile, Hamish returned to his thesis work on the electrochemical properties of ion exchange resins [10].

In an article entitled “Half a Century in Separation Science [13], Hamish wrote

“I had frequently returned to my earliest experiences with ion exchangers in the hope of finding a use for their conducting properties, and as early as 1974 I had proposed using electrically polarized ion exchange beds in IC.” (page 289, paragraph 7)

Hamish proposed an electrically polarized ion exchange resin bed as a suppressor for ion chromatography. The ion exchange resin bed would be “small”, such that electrochemical regeneration would occur between each analysis (or several analyses). For anion analysis using sodium hydroxide as an eluent, the suppressor consisted of a small bed of fully sulfonated cation exchange resin disposed between two porous platinum electrodes. After the suppressor has been used for analysis, the cation exchange resin of the suppressor is primarily in the sodium form. For regeneration, water is pumped in the reverse direction and the suppressor is polarized. Electrolysis (oxidation) of water at the porous platinum anode produces hydronium ions and hydrogen gas. Under the force of the applied electric field, hydronium and sodium ions electro-migrate towards the porous platinum cathode where hydronium ions and hydrogen gas are formed from the reduction of water. This process results in converting the suppressor to the fully regenerated form (hydronium) and produces a waste stream of sodium hydroxide, oxygen and hydrogen. In practice, two of the electrically polarized suppressor columns were used on a valve so when one suppressor was being used for analysis, the other suppressor was electrochemically regenerated using the suppressed eluent as the source of water for regeneration. Dionex filed a patent application describing the electrochemically regenerated packed bed suppressor and a patent [14] issued in 1997. Again, this form of suppression was not commercialized by Dionex, but Alltech Associates Inc. introduced the ERIS 1000 AutoSuppressor based on the electrochemical regeneration of an ion exchange resin bed [15].

During the electrochemically regenerated PBS project, Hamish referenced work from Spiegler [16], Heymann and O’Donnell [17] describing some fundamental electrochemical properties of ion exchange resins. In Figure 1, a cation exchange resin bed in the sodium form is electrochemically converted to the hydronium form by flowing water at the anodic inlet resulting in sodium hydroxide at the cathodic outlet. Electrolysis gases (hydrogen and oxygen) will also be present in this electrochemically produced sodium hydroxide. Hamish suggested that we should investigate this solid-phase (ion exchange resin) approach to electrochemically produce an eluent for ion chromatography.

It was the electrochemically regenerated packed bed suppressor project, that apparently sparked a storm of ideas in Hamish, which he shared with Dionex R&D. Hamish’s ideas would dominate IC research at Dionex in the mid to late 1990s and are still major research and development projects at ThermoFisher Scientific today.

4. Electrolytic eluent generation and suppression: Ion reflux

In 1991, Dasgupta and co-workers [18] were the first to describe a liquid-phase electrodialytic eluent generator to produce a high purity sodium hydroxide eluent for ion chromatography. One configuration of the liquid-phase approach used a flowing stream of sodium hydroxide feed solution on one side of a cation exchange membrane and a flowing stream of deionized water on the other side of the membrane. An anode was disposed on the side of the membrane with the sodium hydroxide feed solution and a cathode on the side with the water. With the application of an applied voltage (constant current), sodium ions from the feed solution would migrate through the cation exchange membrane and into the water stream forming sodium hydroxide. With the cathode disposed in the “product” channel, hydrogen gas is also produced. Due to pressure limitations of the design, the eluent generator was placed on the low-pressure side of the pump (the pump inlet), requiring the hydrogen gas to be removed as not to affect the analytical pump performance. This work clearly demonstrated the feasibility of electrodialytic eluent production using water as well as the ability to perform a sodium hydroxide gradient using a time dependent current profile.

In 1995, during his annual trip to Dionex Sunnyvale (see Figure 2), Hamish and I were in my office and he was “doodling” on the dry erase board. We were discussing polarized resin beds with layers of ion exchange resin, considering polarity and the direction of water flow when suddenly he came up with “the idea of being able to make eluent and recycle it back at the same time”. This was the origin of Hamish’s “Ion Reflux” and was a driving force for electrolytic eluent generation research at Dionex. Hamish returned to Leland and began planning some additional experiments. In a communication from Hamish, he sent the drawing shown in Figure 3 and outlined some critical experiments.

In Figure 3a, a cation exchange resin bed in the potassium form is polarized with an anodic inlet and a cathodic outlet. Water introduced at the inlet will result in the production of potassium hydroxide as the effluent. In Figure 3b, a layer of hydroxide form anion exchange resin is added below the potassium form cation exchange resin. Flowing water through this polarized device will also result in the production of potassium hydroxide as the effluent. In Figure 3c, the position of the anion and cation exchange resin beds are reversed relative to Figure 3b while the liquid flow remains from the anode to the cathode. In his communication, Hamish posed the following question for Figure 3c.
In diagram B, the direction of water flow has been reversed. In this case, potassium hydroxide is produced at the inlet and flows through the potassium form resin bed until it reaches the region of the resin bed in the hydronium form. For every equivalent of potassium, a stoichiometric equivalent of hydronium is formed and at the potassium/hydronium boundary, the potassium hydroxide is neutralized by hydronium. The potassium is exchanged onto the resin and under the force of the electric field, is drawn towards the cathodic inlet. The liquid exiting the resin bed is water with the electrolysis gases. The boundary of potassium and hydrogen forms resin stays fixed in this device and allows for constant eluent concentration and complete suppression. It was this series of experiments which Hamish recognized as a new technique for ion analysis and which he termed “ion reflux”. As Hamish wrote

“I have chosen the term Ion Reflux to denote this continuous circular transport of potassium ion in one phase in one direction and its return in another phase in the opposite direction because of its similarities to refluxing in distillation. In this IC context, Ion Reflux is actually the continuous generation and suppression of KOH.”

In diagram C, Hamish used his invention of a low-capacity anion exchanger, a critical component of the first ion chromatography patent, to create the anion separator function for ion reflux. To make the separator component, the region of the cation exchange resin past the inlet of the ion reflux device is agglomerated with anion exchange latex particles. A variety of approaches were attempted to construct the three distinct regions in the column, and the most practical approach was to use three separate column bodies and couple them as shown in Figure 5. In diagram A, column 1 is the separator, diagram B, column 2 is the suppressor, diagram C shows column 3 which is the eluent generator. Diagram D is the final assembly showing the ion exchange forms of each section. The ion reflux device where eluent generation, separation and suppression all occur in a continuous resin bed, is referred to as IRD-1 (ion reflux device, type 1).

Figure 2. Hamish Small (left) and John Riviello, Dionex Corp, Sunnyvale CA, 1995.

Answering a question about the behavior of a particular configuration of electrically polarized ion-exchange resin beds.

When a bed of cation exchange resin is clamped between porous electrodes, electrically polarized and pumped with water as illustrated below, then the effluent from the bed is a solution of potassium hydroxide.

Figure 3a

\[ H_2O \rightarrow R^-K^+ \rightarrow KOH \]

When a two bed system comprising a layer of potassium form cation exchange resin and a contiguous layer of anion exchange resin in the hydroxide is similarly polarized and pumped (Figure 3b), the product is again potassium hydroxide.

Figure 3b

\[ H_2O \rightarrow R^+K^+R^+OH^- \rightarrow KOH \]

When such a bed as represented by Figure 2 is reversed with respect to flow and polarization, as in Figure 3, the question arises What will happen?

Figure 3c

\[ ? \]
In Figure 6, Hamish represented the complete chromatographic system using Ion Reflux. All the major components of an IC system are used, a pump for the water mobile phase, sample injection valve and a conductivity detector with cell. As shown, a "flow restrictor" is placed at the conductivity cell outlet. The flow restrictor creates backpressure which compresses the electrolysis gas so there is no interference with separation process or conductivity detection. Hamish referred to this as the "Boyles Law Solution" to cope with the electrolysis gas production.

Figure 7 shows one of the first anion chromatograms obtained with ion reflux. The anion separator portion of the ion reflux device used the anion exchange latex of the Dionex AS11 separator column.
These results demonstrated the feasibility of using water as a pumped phase, electrolytically generating an eluent, effecting a separation and suppressing the eluent (to water) using a single polarized resin bed. To some, these results seemed almost too good to be true and for some period in the labs and halls way of Dionex R&D, ion reflux was referred to as “perpetuum mobile” (perpetual motion).

Figure 8 shows the IRD-1 columns used for the first reduction to practice of ion reflux. The column hardware and couplers are composed of PEEK. The stainless-steel tubing at the inlet and outlet of the devices provided the liquid conduit as well the electrical connection to the porous platinum anode and cathode.

While the elegance and the possibilities of the IRD-1 was recognized by the IC enthusiast, Hamish was also quick to acknowledge its limitations. The all-in-one or monolithic aspect of the IRD-1 presented several issues. If one section or components of the device failed, then the complete device would have to be discarded. Given the length of the device (200–300 mm), electrical resistance limited the applied of current, and therefore the concentration of eluent that could be produced and suppressed was limited. To deal with some of these issues, Hamish proposed another version of ion reflux, type 2 or the IRD-2.

5. Evolution of ion reflux

With IRD-2, the idea was to “separate the separator” from the ion reflux device. With IRD-2, electrolytic eluent generation and suppression remained linked, but an external separator column is used. A single cation exchange resin bed is used for the potassium and hydronium ion reservoir. This offered the advantage of simplifying the ion reflux device, shortening the distance between the electrodes which lowers device resistance and increases the eluent concentration range. This provided more options for the chromatographic separation since the separator function is removed from the ion reflux device, so any appropriate separator column to be used. A schematic of an IC system using an IRD-2 is shown in Figure 9.

In IRD-2, a single cation exchange resin bed provides the rechargeable reservoir for both the potassium and hydronium. Compared to the IRD-1, where potassium hydroxide is produced at the cathodic inlet, in the IRD-2, the cathode is displaced from the resin bed using a cation exchange membrane. The small membrane area (about 25 mm²) allows the device to be used on the high-pressure side of the pump and thus withstand the backpressure from the separator column. The anode is placed at the column outlet. An early IRD-2 is shown in Figure 11. Like the IRD-1, the
IRD-2 is gradient compatible. Figure 12 shows a gradient separation of anions using the IRD-2 for eluent generation and suppression with a Dionex AG11 column (4 mm × 50 mm).

A limitation of anion ion reflux is that sample cations are added to the eluent counter-ion (potassium) reservoir, so over time the hydronium reservoirs (suppressor) of the cation exchange resin is diminished. With an IRD-1 device, a hydronium form cation exchange column placed between the injection valve and IRD-1 inlet, will convert the sample cations to hydronium, thus eliminating the addition of cations to the eluent counter-ion generator reservoir and preserving the hydronium reservoir. For the IRD-2, to minimize the effect of sample cations, the sample must be treated prior to the injection valve with a hydronium form cation exchange resin bed to exchange sample cations for hydronium.

With Hamish’s reduction to practice of ion reflux, the concept of electrolytic eluent generation was once again gaining traction at Dionex. Previously, Dionex had worked with manually prepared sodium hydroxide eluents for gradient separations in anion IC. A high-suppression capacity membrane suppressor and new hydroxide selective separator columns had been developed, and some gradient separations had been achieved. One of the challenges was the gradient blank with sodium hydroxide eluents. On paper, hydroxide eluents are ideal since they suppress to water, thus making conductance noise low and analyte response high. In practice, the tendency of sodium (or potassium) hydroxide to absorb ambient carbon dioxide (about 340 ppm in the 1984 and 410 ppm in 2019) made hydroxide gradients a real challenge. Being able to electrochemically produce a sodium or potassium hydroxide eluent using water as the pumped phase seemed ideal as the point-of-use production of the caustic eluent would have little chance to absorb ambient carbon dioxide. A variety of configurations for electrochemical devices to produce eluents were proposed. In addition to ion reflux, Hamish also proposed an electrochemical eluent generation and suppression system that used two resin beds in parallel [20]. Designated as “eluent generation and recycling”, one bed was used to generate eluent while the other bed was used for suppression of the eluent. When the run was completed, the bed used for suppression is now polarized and used to generate eluent, while the bed previously used for eluent generation is now used as the suppressor. Figure 13 shows the details of the configuration.

Much like a suppressor, a resin bed eluent generator must have capacity to be useful for common IC analysis. Early in the research of fully sulfonated cation exchange resin beds for eluent generation, Hamish observed that the empirical capacity was significantly lower than the theoretical capacity. He determined that the was caused by the differences in mobility of hydronium and potassium in the cation exchange

![Figure 12. Separation of common anions using a Dionex AG11 column with an IRD-2. Water flow rate is 1.0 mL/min and uses a current gradient over 7 min (2 mA–20 mA). The sample consist of 1 mM of fluoride, chloride, nitrate, sulfate and phosphate (in order of elution) with a 10 μL injection volume. Reprinted from Ref. [19] by permission from the American Chemical Society.](image1)

![Figure 13. A Dionex-Thermo Fisher Scientific potassium hydroxide eluent generator. Reprinted by permission from Thermo Fisher Scientific.](image2)
resin causing “ion boundary instabilities” [20]. The bulging or “plume” of hydronium into the potassium region of the resin bed resulted in non-Faradaic eluent concentrations as the capacity of the generator was consumed. The configuration of Figure 13 largely solved this problem as the alternating cycle of each polarized ion exchange resin bed acting as a generator then suppressor, refocused the potassium/hydronium boundary thereby depressing the bulge. Meanwhile, Dionex R&D was investigating high-capacity electrolytic eluent generators which could operate uninterrupted for months.

In 2013, ion reflux was revisited by Elkin et al. as an ion chromatographic technique for a field-based instrument [29, 30]. A multi-chamber ion reflux device which incorporated ion exchange membranes to define the chambers was described. Related to Hamish’s IRD-2, the ion reflux device type-3 (IRD-3) offered the advantage of separating the analytical stream from the anode and cathode chambers, thus not requiring any type of degassing of the electrolysis gases. See Figure 10. In addition, since the pumped water phase and electrochemically produced eluent never pass over or through an electrode, detrimental electrochemical by-products are minimized. Unlike the early IRDs, the IRD-3 was not current efficient, but the current efficiency with respect to device build and long-term stability was consistent. An eluent reflux (recycle) device based on a design related to the IRD-3 was also investigated [31].
6. Commercializing electrolytic eluent generation

While extensive work had been done by Hamish and Dionex R&D on packed bed eluent generators (which can also be called solid-phase eluent generators), the first commercial eluent generator introduced by Dionex in 1998 [21] used a static (non-flowing) liquid phase rather than a solid phase for the eluent counter-ion source. The Eluent Generator Cartridge (EGC) was the heart of the Dionex Reagent-Free Ion Chromatography (RFIC) system and offered the IC practitioner the ability to use water as the pumped phase and electrochemically produce an eluent for isocratic and gradient separations [22]. For a potassium hydroxide eluent generator, a concentrated solution of potassium hydroxide was separated from the pumped water using an ion exchange barrier. This barrier (a stack of ion cation exchange membranes) allows for the transport of potassium ions from the liquid counter-ion source into the pumped water stream of the eluent chamber. The reservoir containing the potassium solution (eluent counter-ion) contains an anode and the eluent chamber a cathode. Under the force of an applied electrical potential, potassium ions electromigrate from the reservoir into the eluent chamber and are replaced by hydronium from the anode. The concentration of the potassium hydroxide eluent produced is directly proportional to the applied current and inversely proportional to the water flow rate. The EGC is placed on the high-pressure side of the pump (between the pump outlet and the injection). The potassium hydroxide produced in the eluent chamber also contains hydrogen gas as shown in Figure 14. A methane sulfonic acid EGC for cation IC was also introduced in 1998.

The coupled production of the eluent and electrolysis gases in the EGC requires degassing of the newly formed eluent prior to the injection valve. For the EGC devices described above, a gas permeable, but liquid impermeable polymeric tubular membrane is placed at the outlet of the eluent generator [23]. In the initial embodiment of this degasser, the eluent containing the electrolysis gas would flow through the lumen of the tubular membrane and the gas would diffuse out through the wall of the membrane. Since the tubular degassing membrane is in the high-pressure flow path of the analytical column, the tubular membrane must be able to withstand significant back pressures (at least 3000 psi). As the size of the resin particles of the IC analytical columns have decreased in order to improve chromatographic performance (higher efficiency, improved resolution or potentially faster run times), the flow of the degasser was modified such that the eluent flows on the outside wall of the tubular membrane and the electrolysis gas diffuses into the center lumen. The direct contact of the electrode in the eluent chamber not only necessitates a degasser, but there are electrochemical by-products formed that can be detrimental to downstream components of the chromatographic system [24].

7. Eluent regeneration - another look at ion reflux

In 1998, with ions refluxing and recycling and Dionex’s collaboration with Hamish, it was recognized that the electrodialytic membrane suppressor that Dionex had commercialized in 1992, was itself, an ion reflux device. The Dionex Anion Self Regenerating Suppressor (SRS) consist of two cation exchange membranes with a gasketed ion exchange screen that is sandwiched between the two membranes. The membranes define the low-volume eluent channel as shown in Figure 15. On the other side of one membrane is an anode chamber with an anode. Similarly, on the other membrane, a cathode chamber containing a cathode. For this example, a sodium carbonate/sodium bicarbonate eluent will be used, but the argument also applies for a sodium or potassium hydroxide elu- ents. The sodium carbonate/sodium bicarbonate eluent exits the eluent chamber of the suppressor as carbonic acid with the analytes and is directed to the conductivity detector cell. From the conductivity cell, the suppressed eluent is directed back to the electrode chambers of the suppressor (referred to at Dionex as suppressor recycle mode) where water of the suppressed eluent in the anode chamber is oxidized to generate hydronium ion (and oxygen gas) for suppression. In the cathode chamber, water is reduced to hydroxide (and hydrogen gas) to provide electrical neutrality for the eluent cation (sodium). On paper, and at equilibrium, what appears to exit the electrode (or regenerant) chambers is the original eluent (sodium carbonate/sodium bicarbonate) with trace analyze anions, oxygen and hydrogen. The recycled or regenerated eluent...
can be sent back to the eluent bottle. This is reminiscent of Hamish’s ion reflux as this system provides for “continuous generation and suppression” of eluent, but does require a manually prepared eluent.

In practice, continuous eluent generation using an electrodialytic membrane suppressor is more challenging than the paper experiment. The main problem was eventually identified as the accumulation of electrochemical products such as hydrogen peroxide, ozone and possibly percarbonate in the regenerated eluent. These oxidizing agents damage the anion exchange sites of the ion chromatography column, resulting in a reduction in analyte retention time and poor chromatographic efficiency. In addition, the eluent is slightly more concentrated because of the small volume of water that is electrolyzed in the electrode chambers. With each sample injection, a sample loop volume of eluent is removed from the system and replaced with sample which eventually results in a minor dilution of the eluent. Diligent researchers at Dionex were able to solve these issues, and a product, the RFIC-ER (Reagent-Free Ion Chromatography-Eluent Regeneration) was introduced in 2006 [24]. The system uses a plurality of traps and columns to purify the eluent and eliminate the electrolysis gases prior to re-introduction in the eluent bottle as shown in Figure 16. Since RFIC-EG uses a manually prepared eluent, it is not compatible with gradient separations since there is only a single eluent and the eluent is reformed in the suppressor before being sent to the eluent bottle. Like its cousin, ion reflux, the accumulation of sample eluent counter-ions limits the lifetime of the eluent. Depending on the sample type and volume, the manually prepared eluent of the RFIC-ER requires replacement every two to four weeks.

Troviron Singapore Pte. Ltd patented an electrolytic eluent regeneration system [25] in which the electrode chambers are separated from the eluent regeneration and suppression chambers using ion exchange membranes. In this device, no electrolysis gas or electrochemical by-products are produced in the recycled eluent stream. A separate source of deionized water for production of the eluent counter-ion (hydronium or hydroxide) and the suppression ion (hydronium or hydroxide) is recycled through the electrode chambers.

8. Returning to suppression

Another suppression product that was inspired by Hamish’s polarized ion exchange resin beds was a continuously regenerated packed bed suppressor [26]. The initial concept was based on a polarized ion exchange resin bed, but rather than having the electrodes in direct contact with the resin, ion exchange membranes would be used to separate the electrodes from the resin bed. This would isolate the analytical stream from the electrode chambers (prior to the conductivity cell), thus no electrolysis gases would be present in the suppressed eluent. The scope of the “continuously regenerated packed bed suppressor” project involved developing suppressors for both anion and cation isocratic IC applications. Instead of using conventional ion exchange resins in these suppressors, ion exchange monoliths based on irradiation grafting of styrene (for cation exchange) or vinyl benzyl chloride (for anion exchange) monomers on sintered polyethylene were used as shown in Figure 17. Ion exchange membrane flow distributors are placed between the ion exchange monolith discs to increase the eluent flow path which improves suppression capacity. The Atlas suppressors were introduced by Dionex in 2002.

During Hamish’s 1999 annual visit to Dionex, he investigated polarized ion exchange resin beds for the removal of carbonate and trace anions from hydroxide eluents. The Dionex KOH eluent generator was a new product and while the advantages of using deionized water to electrochemically generated potassium hydroxide and implement gradients well recognized, carbonate was still a nagging contaminant. In addition, the ionic contamination of the deionized water used for eluent generation was a factor in the purity of the electrochemically generated eluent. Using various hardware designs from the IRD-2 project, Hamish demonstrated the ability of to reduce carbonate and other anionic contaminants in potassium hydroxide solutions ranging in concentration from 1-75 mM. This work eventually resulted in the Dionex “Continuously Regenerated Trap Column (CR-TC) which is used with the Dionex EG systems to “purify” the electrochemically generated eluent prior to the injection valve [27].

9. The electrochemical pump

With electrolytic eluent generation and suppression now well established in ion chromatography, Hamish revisited some curious properties of electrolytic ion exchange that were observed from his early work. All ions in an aqueous solution are hydrated. As they electromigrate under the force of an applied potential, not only is the ion moved, but so is the water associated with hydration of the ions. He considered the electromigration of an ion through an ion exchange membrane in which the membrane has low water permeability and asked the question to what degree would water be transported across the membrane with the hydrated ion and can water movement be controlled by the applied potential? In 2008, a patent application was filed on what Hamish referred to as the “electrochemical pump” (ECP) [28]. In Figure 18, a central water generator compartment is disposed between an anode compartment on one side and a cathode compartment on the other side. The water generator compartment is defined by an anion exchange membrane on the cathode side and a cation exchange membrane on the anode side. With water in the electrode compartments and with the application of voltage, hydronium ions produced at the anode are driven through the cation exchange membrane towards the cathode and into the water generator compartment. In a similar fashion, hydrated hydroxide ions produced at the cathode are driven through the anion exchange membrane towards the anode and into the water generator compartment. In the water generation compartment, the hydronium and hydroxide combine resulting in a bulk production of water. For every milliamp of applied current, about 40 nL of water per minute was produced. A linear relation of current and flow was demonstrated from about 2-100 mA. The maximum flow with the ECP was about 5 µL/min which is suitable for capillary liquid chromatography. Hamish demonstrated that the electrochemical pump could operate at backpressure up to 1200 psi (and potentially higher depending on the hardware design). With the initial hardware design, bulk leakage of water through the membrane at elevated pressure reduces the electrochemically pumped water flow by about 10%.

Hamish noted that the conductance of the electrochemically formed water of the electrochemical pump was typically several hundred microsiemens which he determined to be from common ionic contaminants in the deionized water in the electrode chamber. In addition to the hydronium and hydroxide ions from the electrode chambers electromigrating into the water generator compartment, trace ions in the deionized water feed also electromigrate into the water generation chamber. Hamish recognized this as an electrochemical means to concentrate trace ions from deionized water. The concentrated ions in the water generator could then be directed to an ion chromatograph for analysis.

10. Some final thoughts

Hamish’s 62 years of ion exchange invention and innovation has forever changed the world of ion analysis. From the first successful ion chromatogram generated November 9th, 1971 to the tens of thousands of ion chromatographs being used around the world today, Hamish’s scientific curiosity and his perception of problems as opportunities have sustained the evolution of ion chromatography. While this paper highlighted the electrolytic ion exchange contributions from Hamish, his foundational work in low-capacity ion exchange resins remain at the separation heart of ion chromatography. There have been significant advancements in ion chromatography stationary phases since the
invention of IC, but the original surface sulfonated resins coated with anion exchange latex are as important today as they were 50 years ago.

Hamish continued his research in until 2013, at which time he retired from ion exchange and consulting for Thermo Fisher Scientific/Dionex. He remained active in his basement investigating new ways to measure flow and volume (returning to research he had done at Dow Chemical in the 1970's on flow monitoring). Hamish and I had frequent Skype calls to catch up and discuss his research and our collaboration. I would visit Hamish and his wife Beryl at least once a year in Ashland Oregon. The photo of Figure 19 was taken during a visit in 2015. I was fortunate to catch up and discuss his research and our collaboration. I would visit Hamish and his family the week prior to his passing (August 20th, 2019) and we had the opportunity to talk about our many years of collaboration and friendship. It was truly a special time, and one that I will carry with me all my days.

Hamish left an indelible mark on my career and he has enriched my life in innumerable ways. I feel fortunate to have had a 36-year friendship with a truly great scientist, and most importantly, an exceptionally decent and compassionate human being.

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