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New membrane-based electrolytic suppressor device for suppressed conductivity detection in ion chromatography

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ABSTRACT

This paper discusses the newest advancement in chemical suppression preceding conductivity detection. The new suppressor uses electrolysis of deionized water to generate the required acid or base for the suppression neutralization reaction and utilizes the electrical field to enhance, through electrodialysis, the suppressor's capacity for neutralization. The suppressor is able to accommodate eluents as high as 150 m*M* NaOH, without the need for a separate regenerant solution, by recycling the conductivity detector cell waste to the regenerant and electrolyzing the water in the waste stream to the required acid or base. The device is able to use deionized water as regenerant and neutralize the eluent stream to deionized water without the expected increase in resistance by employing ion exchange material in intimate contact with the electrodes and the membranes. The current is carried with low resistance through the ion-exchange material via ion transport from one ion-exchange site to another.

INTRODUCTION

Ion chromatography (IC) has developed into a strong analytical technique from its meager beginnings as a method to determine chloride and sulfate. Today IC uses a variety of detectors and a variety of separation modes to analyze for inorganic and organic ions in a broad range of matrices. The common thread for ion chromatography is the use of ion-exchange media to separate the ions of interest in the matrix. The original detection scheme, chemically suppressed conductance detection, is still the mainstay method of detection for IC.

Chemically suppressed conductance involves the use of weak acid or weak base salts as eluents for the elution of anion and cations, respectively, followed by chemically exchanging eluent ions, by means of an ion-exchange resin or membrane, for hydronium ions (anion determination) or hydroxide ions (cation determination). This causes decreased conductance from the eluent because the eluent is a weak acid or base and therefore weakly ionized, and increases the detector conductance signal for the strong acid or strong base analytes by pairing them with highly conducting hydronium ions (anion determination) or hydroxide ions (cation determination). It has been said that the suppressor turns the bulk property conductivity detector into a solute specific detector.

Suppressors have developed from the first, so called, packed-bed suppressor, described by Small *et al.* [1] to continuously regenerated membrane based suppressors. The first membrane-based suppressor was the fiber suppressor [2], a tubular shaped ion-exchange membrane continuously bathed with dilute sulfuric acid regenerant. This was followed by the MicroMembrane suppressor [3], which was composed of a thin (< 0.075 mm) flat ion-exchange membrane in intimate contact with ion-exchange screens in the eluent and regenerant chambers to maximize suppression capacity and minimize dispersion.

This paper describes an electrochemical suppressor which takes advantage of the evolution of suppressors and combines electrodialysis and electroly-

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sis to create the best-performance lowest-maintenance suppressor for IC with suppressed conductance detection. General construction, theory of operation, modes of operation and performance are discussed.

EXPERIMENTAL

Chromatography system

The chromatography systems used in this study were Dionex DX-300 and System 4500i ion chromatographs. The DX-300 uses a Dionex AGP quaternary gradient pump fitted with pistons to generate flow-rates compatible with either 2 or 4 mm I.D. columns. The System 4500i is equipped with a Dionex GPM-2 quaternary gradient pump. Detectors for these systems were a Dionex CDM-II conductivity detector and a Dionex pulsed electrochemical detector operating in the conductivity mode. All data were collected and processed on Dionex AI-450 software.

Columns

Separation columns for this work included the Dionex IonPac CS12 for cation determinations and Dionex IonPac AS4A-SC, AS5A and AS9-SC columns for anion separations.

Chemicals

Methanesulfonic acid (MSA) eluents for cation determinations were prepared from the 99+% puriss. acid (Fluka, Ronkonkoma, NY, USA). Hydroxide eluents for anion separations were prepared by dilution from the certified grade 50% solution (Fisher, Pittsburgh, PA, USA). Carbonate–hydrogencarbonate eluents were prepared from a commercially available mixed concentrate (Dionex, Sunnyvale, CA, USA). Deionized water (18 MΩ) was obtained from a Millipore (Bedford, MA, USA) Milli-Q water purifier.

RESULTS AND DISCUSSION

Mechanism of suppression

Chemical suppression for IC serves two purposes. The first is the most familiar, lowering the background conductance to a low level, which reduces the system noise. Equally important is enhancement of the overall conductance of the analyte. These two factors together serve to greatly enhance the signal-to-noise ratio for suppressed IC.

The general mechanism of suppression is outlined in Fig. 1. This is shown for the anion separation case, although the cation case is completely analogous. The highly conductive eluent (NaOH) passes through the column, then encounters hydronium ions on the ion-exchange sites in the suppressor. The hydronium ion neutralizes the eluent, forming a weakly conducting species (water) and the counterion form of the ion-exchange site. Analytes passing through the suppressor interact similarly. The analyte counterions exchange for hydronium ions, forming very highly conducting species as hydronium ions have the highest specific conductance of all ions. The net result is a very strong signal superimposed on a low-noise background, giving a very favorable signal-to-noise ratio. For cations, the analogous situation uses hydroxide neutralizing an acidic eluent as well as exchanging for the anionic portion of the analyte.

History of chemical suppression

Packed bed suppressors

Chemical suppression for IC was first conceived by Small *et al.* [1] at Dow Chemical Company in 1975. To reduce the background conductance due to the eluent, they placed a second ion-exchange column between the separator column and the conductivity cell. This second column, originally called the "stripper" column by the inventors, was a simple, yet elegant solution to a difficult problem.

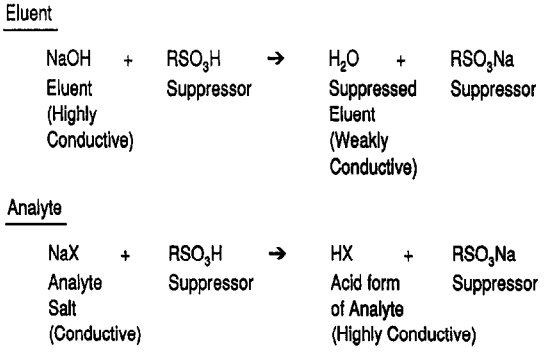

Fig. 1. General mechanism of suppression for anion determinations.

These original suppressors consisted of large columns containing strong acid cation-exchange resin in the hydronium ion form. For anion analysis, alkali metal salts of weak bases were chosen as eluents. As the eluent entered the suppressor, the weak base anion reacted with hydronium, neutralizing the species. Simultaneously, the alkali metal counterion would occupy the ion-exchange sites freed by the hydronium. This served to greatly reduce the conductometric background. As with all suppression, the analyte counterions also exchange for hydronium, serving to greatly enhance the conductivity signal. Cation analysis was completely analogous, using mineral acid eluents and anion exchange resin in the suppressor.

The advent of the packed bed suppressor allowed the use of detection specifically geared toward ions, namely, conductivity. Before chemical suppression, conductivity was seldom used because it is a bulk property detector, subject to being "swamped out" by the background signal due to the ionic eluent. With the first suppressors, conductivity became a sensitive and specific detection scheme for ions of all types.

The original packed bed suppressors had some major drawbacks. To contain enough resin to be feasible, the suppressors had a very large dead volume, on the order of 1500 μl. This in turn caused considerable peak dispersion and broadening. At the time, however, this was not a major problem because the separation columns available had low efficiency thus were not greatly affected by the dead volume of the suppressor. The other problem was regeneration of the bed. After several hours of analyses, the bed became expended, *i.e.* all of the ion-exchange sites were in the counterion form rather than hydronium or hydroxide. The column had to be regenerated off-line with acid or base (depending on the type of suppressor), flushed with water, and then placed back on-line. While this process could be automated to some degree, it was still a source of annoyance and did not allow around the clock operation. Another problem was the analysis of weakly ionized species such as organic acids. These neutral organic acids (that have been neutralized in the suppressor) could penetrate the Donnan membrane (which excludes ionic species) of the protonated ion-exchange sites and interact by inclusion in the suppressor resin phase with the stationary phase. As the suppressor became expended, the organic acids would deprotonate, thus causing a change in peak height and shorter retention times [4].

Despite these problems, the packed bed suppressor made IC a viable commercial technique. The first commercial IC with packed bed suppression was sold by Dionex in 1975. IC proved to be a very valuable analytical technique, especially for anion analysis. Previously, the wet methods for inorganic anions such as chloride, nitrate, and sulfate were time consuming, labor intensive and not particularly sensitive. These methods were based largely on such techniques as titration, colorimetry and gravimetry. No methods existed that had detection specific to the analytes of interest; most of these techniques used bulk properties such as pH or precipitation reactions that are highly subject to interference. IC immediately improved this situation by being able to do all of the ions in a single run, was sensitive, specific and amenable to automation. The cation version originally required runs of the monovalent ions separately from the divalents, however, both were reasonably rapid and sensitive.

Fiber suppressors

To combat some of the drawbacks with the packed bed suppressors, Stevens *et al.* [2] at Dow developed the hollow-fiber suppressor in 1981. This was the first membrane-based suppression device. The fiber suppressor consisted of a long, hollow fiber made of semi-permeable ion-exchange material. Eluent passed through the hollow center of the fiber, while a regenerating solution bathed the outside of the fiber, allowing for continual replacement of the regenerant ion as the eluent passed through. The main advantage of this design was that it allowed for continuous operation of the chromatography system. There was no need to take the suppressor off-line for regeneration as with the packed bed devices.

Operation of the fiber suppressors is as follows. The eluent, for this example sodium carbonate, passes through the center of the fiber, which is bathed with a sulfuric acid solution counter-current to the eluent to provide hydronium ions for the suppression reaction. The cation-exchange sites in the fiber permit the transfer of hydronium ions to neutralize the carbonate to the weakly ionized carbonic acid. Sodium ions from the eluent are transported out

through the cation-exchange sites in the fiber to the regenerant solution, forming a sodium hydrogen-sulfate solution. The regenerant solution constantly flows at several ml/min to remove the sodium ions. Operation of the cation version used anion-exchange fibers, mineral acid eluents and hydroxide as the regenerant solution.

Fiber suppressors offered several advantages over the packed beds beside continuous operation. Dead volumes for these devices were on the order of 300 μl, considerably lower than the packed bed types. This gave more efficient chromatographic peaks, which was useful because column technology had advanced significantly in the six years since the advent of IC. As columns became more efficient, the need for more efficient suppressors arose. Also, Donnan forces which wreaked havoc with weakly ionized species were greatly reduced, thus determination of these analytes became more reliable.

Fiber suppressors were limited in their ability to suppress fast flow-rates (>2 ml/min) or high concentration (>0.005 *M*) eluents. Their suppression capacity relative to packed beds was considerably lower. It had been found that laminar flow in the hollow fiber prevented good mass transport of the eluent ions to the walls of the fiber, resulting in significant band broadening. A solution to this problem was to pack the fiber with neutral resin beads to promote tortuous flow to the walls, with much improved band broadening [5].

Membrane suppressors

The drawbacks with the fiber suppressors proved limiting to the growth of IC. Separation column technology was advancing rapidly; there was a strong desire to perform different analyses in more varied matrices. At the time, gradient IC was not possible due to the lack of suitable suppression. To take advantage of these advances, a new suppression device with much higher capacity and lower dead volume would be necessary, yet still able to operate around the clock with minimal supervision. A flat membrane suppressor, known by the trade name MicroMembrane suppressor (MMS) from Dionex, proved to have all of these attributes upon introduction in 1985 [3].

Design of the MicroMembrane incorporates two semi-permeable ion-exchange membranes sandwiched in between three sets of ion-exchange screens as depicted in Fig. 2. The eluent screen is a fine-mesh ion-exchange screen that promotes the suppression reaction while occupying very little volume. Ion-exchange membranes on either side of the eluent screen define the eluent chamber. These membranes allow passage of the regenerating ion in and the eluent counterion out of the eluent chamber in much the same manner as described for the fiber suppressor. There are two regenerant screens, both ion-exchange functionalized, that permit tortuous flow of the regenerant solution towards the membranes. These screens provide a reservoir for suppressing ions, essentially at molar concentrations, directly at the membrane without having counterions present. One of the drawbacks of the fiber suppressor was that the regenerating medium directly bathed the membrane, which led to counterion leakage into the eluent chamber, causing higher background and noise. With functionalized ion-exchange screens in the membrane suppressor, counterion leakage is greatly reduced and suppression capacity is increased to more than 25 times that of a fiber device.

The flow pattern for the anion suppressor is shown in Fig. 3. The eluent, the sodium salt of a weak acid (in this example, sodium hydroxide) flows into the eluent chamber. A mineral acid such as dilute sulfuric acid is flowing counter-current to the eluent at approximately 3–10 times the chromatographic flow-rate. Cation-exchange membranes permit the flow of hydronium ions from the

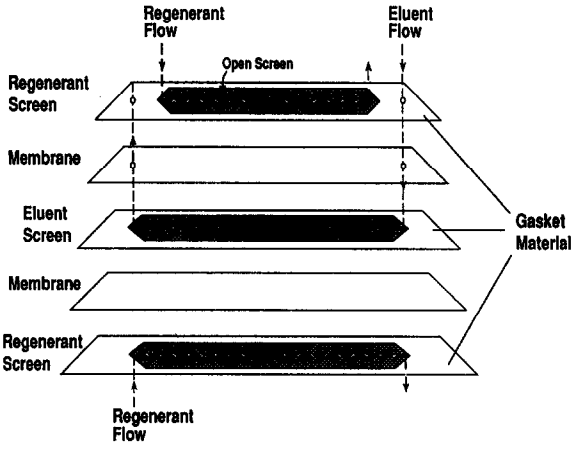

Fig. 2. Internal design of the MicroMembrane Suppressor.

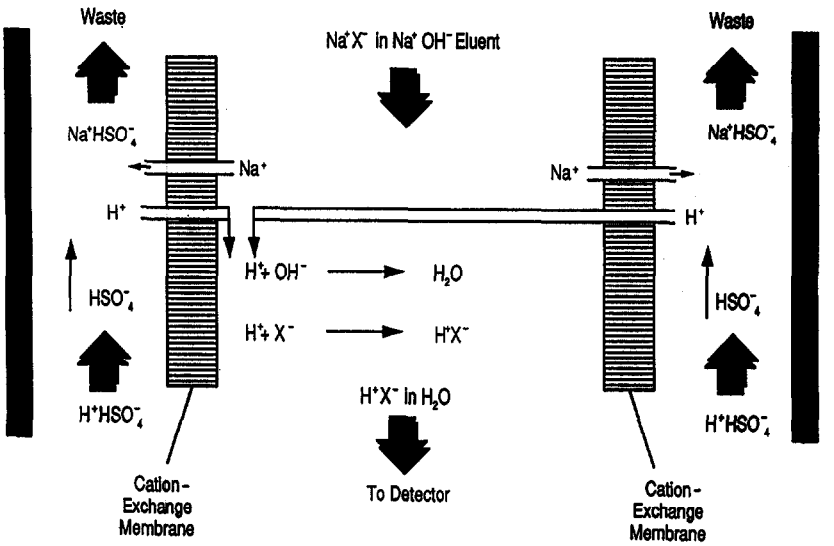

Fig. 3. Suppression mechanism of the Anion MicroMembrane Suppressor.

regenerant chamber to the eluent chamber. The hydronium ions neutralize the hydroxide to its weakly ionized form (water). The sodium counterions transport from the eluent to regenerant chamber to maintain electronic neutrality in the regenerant solution. These are then swept out with the regenerant solution waste. Conductivity enhancement of the analyte ions occur in much the same fashion. The counterions to the analyte exchange through the cation-exchange membrane with hydronium ions, thus creating a significantly higher conductometric signal.

Fig. 4 represents the cation suppressor case. Mineral acids, strong organic acids, and amino acids are commonly used as eluents. In this example, HCl is the eluent. The regenerant flowing counter-current

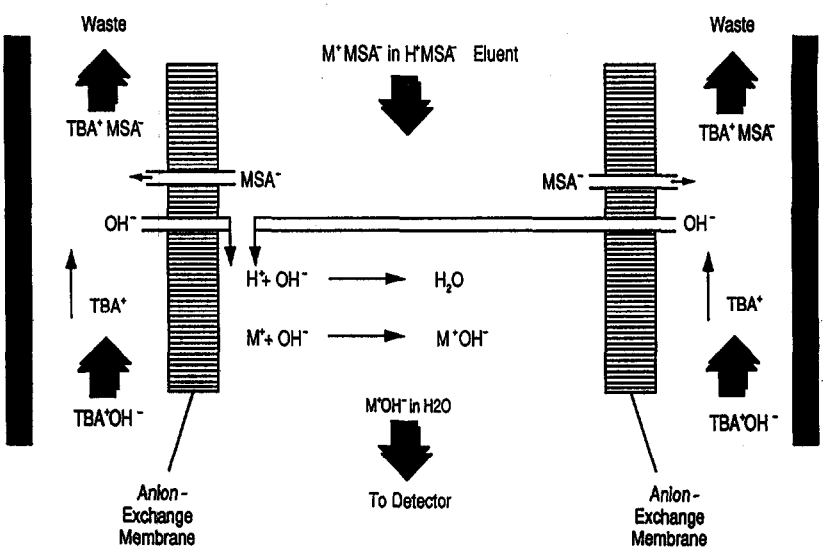

Fig. 4. Suppression mechanism of the Cation MicroMembrane Suppressor.

to the eluent is a strong base such as tetrabutylammonium hydroxide (TBAOH). Anion-exchange membranes permit the exchange of hydroxide from the regenerant chambers with the eluent counterions. Hydroxide ions traverse the membrane and neutralize the hydronium ions from the eluent. Simultaneously, chloride ions leave the eluent chamber to the regenerant chambers to maintain charge balance, which are removed by the liquid flow. For the analyte, the anions are exchanged with hydroxide ions to enhance the conductivity of the analyte.

The design of the MicroMembrane Suppressor addresses many of the problems of the previous suppressors. Eluent passes through a chamber that is defined by an ion-exchange screen sandwiched between two membranes, thus the dead volume is very low, on the order of 50 μl, roughly 1/6th that of the fiber suppressors and more than an order of magnitude smaller than the packed beds. This allows very efficient peaks, greater than 8000 theoretical plates per column.

Membrane suppressors have much greater suppression capacity as well. Suppression capacity is defined as the number of equivalents of eluent ion that is suppressible per unit time. Due to the low dead volume, a high linear velocity is maintained inside the suppressors, which allows for efficient transfer of ions through the membranes. This leads to suppression capacities of 200–300 μequiv./min, significantly higher than that for the previous suppression devices.

Concentration gradients are possible with membrane suppressors [6]. This has proved to be a very useful tool for analytical chemists. By changing the eluent concentration over time, one can elute ions that are tightly held on the column. Membrane suppressors can handle steep gradient ramps due to continuous regeneration of the eluent chamber and high dynamic capacity. As a demonstration of the gradient capability of suppressed IC, a standard containing 35 anions can be eluted with a sodium hydroxide gradient in less than 30 min (see Fig. 5). The MicroMembrane suppressor also allows the use of organic modifiers in the eluent to further mediate the analyte retention on the column. Multiphase analytical columns have been developed that have the ability to control ion-exchange and adsorption or ion-pair retention with use of organic solvents [7].

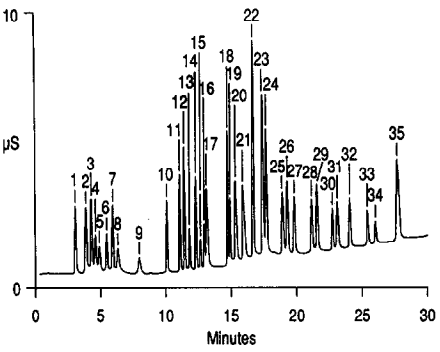

Fig. 5. Gradient separation of inorganic and organic anions. Column: AS5A. Suppression: ASRS, cell effluent recycling. Eluents: (E1) 0.75 m*M* NaOH, (E2) 200 m*M* NaOH. Flow-rate: 1.0 ml/min. Gradient program (E1–E2): 0 min (100:0), 5 min (100:0), 15 min (85:15 min), 30 min (57:43). Peaks: 1 = fluoride; 2 = acetate; 3 = α-hydroxybutyrate; 4 = butyrate; 5 = gluconate; 6 = α-hydroxyvalerate; 7 = formate; 8 = valerate; 9 = pyruvate; 10 = monochloroacetate; 11 = bromate; 12 = chloride; 13 = galacturonate; 14 = nitrite; 15 = glucuronate; 16 = dichloroacetate; 17 = trifluoroacetate; 18 = phosphite; 19 = selenite; 20 = bromide; 21 = nitrate; 22 = sulfate; 23 = oxalate; 24 = selenate; 25 = α-ketoglutarate; 26 = fumarate; 27 = phthalate; 28 = oxalacetate; 29 = phosphate; 30 = arsenate; 31 = chromate; 32 = citrate; 33 = isocitrate; 34 = *cis*-aconitate; 35 = *trans*-aconitate.

One of the major drawbacks of the membrane suppressors was that they required a constant flow of regenerant to provide continuous suppression. This could consume large volumes (up to 10 ml/min) of regenerant, necessitating large reservoirs of the chemicals needed for suppression. A device introduced in 1987 circumvents this problem. The AutoRegen accessory developed by Dionex allows for continuous regenerant recycling. A large ion-exchange cartridge is used to remove the suppression waste products such as eluent counterions and replace it with fresh regenerating ions. A pump recirculates the regenerant through the suppressor and the cartridge. This requires only a small reservoir of regenerant for effective operation. For example, in anion suppression, sulfuric acid is used for regeneration. The suppression product is sodium hydrogensulfate. Sodium ion is caught on a cation-exchange bed in the hydronium form and exchanged for hydronium ion. This serves to insure a fresh supply of regenerant solution for the suppressor. This device allows full around the clock oper-

ations as the cartridges can last several weeks before replacement. On-line IC systems in particular benefit from regenerant recycling [8].

Microbore membrane suppressors for IC were introduced in 1991. Microbore HPLC (column internal diameters up to 2 mm) has been around since the inception of HPLC [9]. One problem with microbore HPLC and UV–Vis detection is the loss of mass sensitivity with conventional detector cells [10]. Microbore IC with 2 mm I.D. columns and suppressed conductivity detection has no loss of sensitivity because conductivity is not mass dependent. Microbore IC has the other advantages of low sample volume, low flow-rate and reduced waste.

One important advantage of the microbore membrane suppressor is greatly enhanced suppression capacity. The microbore MicroMembrane suppressor has been scaled down to reduce dispersion relative to its larger cousin, the original suppressor designed for 4 mm I.D. columns. As shown in Fig. 6, the overall internal volume has been decreased by a factor of 3 to 4 to maintain the same linear velocity as found in the 4 mm versions. If the regenerating solution flow-rate is maintained at the same 3–10 ml/min, a greater eluent counterion concentration gradient is maintained between the eluent and regenerant chambers, leading to higher suppression capacity. Suppression capacity for microbore systems are 2–3 times greater than the 4 mm analogues. This allows greater concentration eluents to be used, which in turn expands the types of analyses that can be performed, such as the analysis of a number of polyphosphates ions in polyphosphoric acid (see Fig. 7).

Alternative modes of chemical suppression

There have been some other suppression schemes mentioned in the literature. Chelation by a transition metal form ion-exchange resin of a chelating agent has been suggested as an effective form of chemical suppression [11]. For this system, the potassium salt of ethylenediamine diacetic acid (EDDA) was used as the eluent, and a cation-exchange bed in the copper form was the suppressor. As eluent entered the suppressor, EDDA chelated with Cu(II) ions, forming a neutral species that was trapped in the resin matrix. Analyte counterions passing through the suppressor would also exchange for copper. This device gave relatively low backgrounds on the order of 5 μS/cm, however due to the counterion exchange for the rather weakly conducting Cu(II) ion, sensitivities would not be as

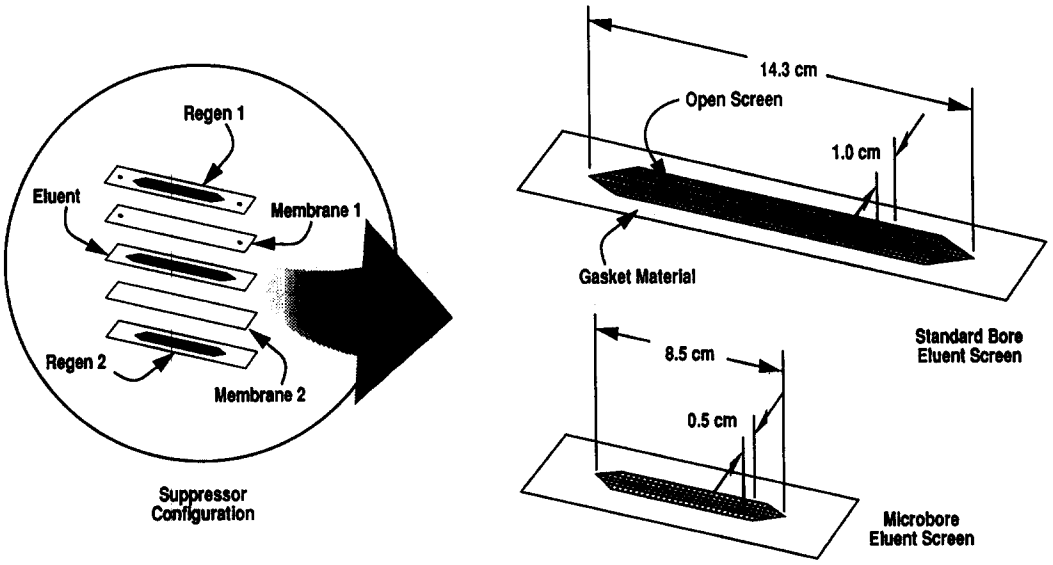

Fig. 6. Internal dimensions of microbore *vs.* standard bore MicroMembrane Suppressors.

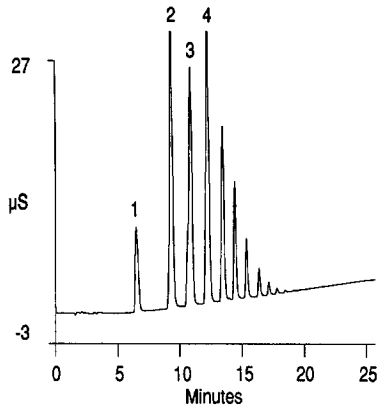

Fig. 7. Separation of polyphosphates in polyphosphoric acid. Column: PAX-100. Eluent: 40–300 m*M* NaOH in 20 min with 5% methanol at 0.25 ml/min. Suppression: ASRS with chemical regeneration. Peaks: 1 = orthophosphate; 2 = pyrophosphate; 3 = tripolyphosphate; 4 = tetrapolyphosphate.

good as for suppressors that use neutralization chemistry which exchange for highly conducting hydronium ion.

Electrochemical suppression

Since the early days of chemical suppression, attempts have been made to use an electric field to improve ion transport through ion-exchange membranes with electrodialysis. The logic for using an electric field would be to provide an extra "push" for the ions in the suppression reaction by driving the neutralizing ions (such as hydronium in a suppressor for anion chromatography) with an electrode of the same charge, and attracting the counterions to an oppositely charged electrode to facilitate removal.

Tian *et al.* [12] have constructed a suppressor that uses electrodes separated from a resin-packed eluent chamber by cation-exchange membranes. The authors claim the main feature of this device is the use of a static regenerant solution of 100 m*M* sulfuric acid using a current of 50 mA and a cell voltage of 4 V. The contention is that application of the electric field helps remove sodium ions from the eluent chamber. It is not mentioned, however, if the device would work in the absence of electrical current. With a high concentration of sulfuric acid on one side of a cation-exchange membrane, it is quite likely that a simple concentration gradient would allow diffusion of hydronium ions in the manner of the membrane based suppressors. Also unclear is the fate of the sodium ion buildup in the regenerant chamber —if a static regeneration solution is used, then eventually this suppressor would become expended when the sodium ions in the regenerant chamber approach equilibrium with those in the flowing eluent stream.

The patent literature teaches of a similar device using flat membranes with electrodes [13]. Similar to the device of Tian *et al.*, flowing sulfuric acid is used as electrolyte in the regeneration chambers, in this instance separated from an open eluent chamber by two cation-exchange membranes. Typical operating conditions were a current of 120 mA at a voltage of 200 V. A similar device was developed by Ban *et al.* [14], using a tubular design with HCl as the regenerant solution. In each of these suppressors, it is claimed that the electric field is used merely as a "pusher", that is, an aid to ion mobility through the ion-exchange membrane. However, one cannot have charged electrodes with no current passing between them; ions can conduct the current between the electrodes, but redox chemistry must be occurring at the electrode surfaces to complete the circuit. This suggests that electrochemistry, not electrodialysis, is the main driving force of electrolytic-type suppressors. In fact, it has been shown that the presence of sulfuric acid in the regenerant chambers of an electrolytic suppressor has a deleterious effect on overall suppression [15]. Electrochemical suppressors which operated without the presence of external acid or base will be discussed in the next section.

The well-known electrolysis of water produces the chemical reactions as outlined in eqns. 1 and 2.

$$\text{Anode:} \quad 3\,H_2O \rightarrow 2\,H_3O^+ + 1/2\,O_2 + 2\,e^- \quad (1)$$

$$\text{Cathode:} \quad 2\,H_2O + 2\,e^- \rightarrow 2\,OH^- + H_2 \quad (2)$$

These reactions are quite facile, especially at metal surfaces with low overpotentials such as platinum [16]. Since hydronium and hydroxide ions are generated in these reaction, it is possible that with the correct ion-exchange membranes, one can utilize the ions for suppression [17]. Thus, a suppressor for anion analysis uses generated hydronium ion with cation-exchange media to neutralize a basic eluent,

and a cation version uses hydroxide ion with anion-exchange sites.

Strong and Dasgupta [15] designed the first practical suppressors to use water electrolysis. They used single-membrane and double-membrane helical designs for their units. A peristaltic pump was used to deliver water as the regenerant source. They were able to suppress up to 200 m*M* sodium hydroxide eluents, and demonstrated good gradient chromatography for anions.

New electrolytic suppressor for IC

In 1992, Dionex introduced the first commercial electrochemical suppressor, which they named the "Self Regenerating Suppressor", or SRS [18]. A flat membrane design similar to their membrane suppressor was used as the suppression means, with two platinum electrodes incorporated into the design that allow electrolysis of water to occur. A constant current power controller generates the electric field for the electrolytic reaction. One significant feature of this design is that it allows the use of very low flow-rates for the regenerant water, to the point where the suppressor can use the deionized eluent after suppression from the detector cell waste as its water source, greatly simplifying the plumbing scheme and reducing waste (see below). Since water electrolysis is utilized as the regenerant ion source, no independent chemical feed is necessary as was needed for past suppression devices.

The internal design of the suppressor is shown in Fig. 8. Functionalized ion-exchange screens are present in the regenerant chambers to facilitate electric current passage, with permselective ion-exchange membranes defining an eluent chamber containing another functionlized ion-exchange screen to minimize dead volume. Two platinum electrodes are placed in the regenerant chambers, one between a regenerant screen and the hardware shell, and another between the membrane and the other regenerant screen. This electrode placement proved optimal for current efficiency and removal of the waste gases.

The neutralization reactions occurring in the SRS are similar to those of the membrane-based suppressors. For anion-exchange chromatography, using the Anion Self Regenerating Suppressor (ASRS), hydronium ions generated at the anode

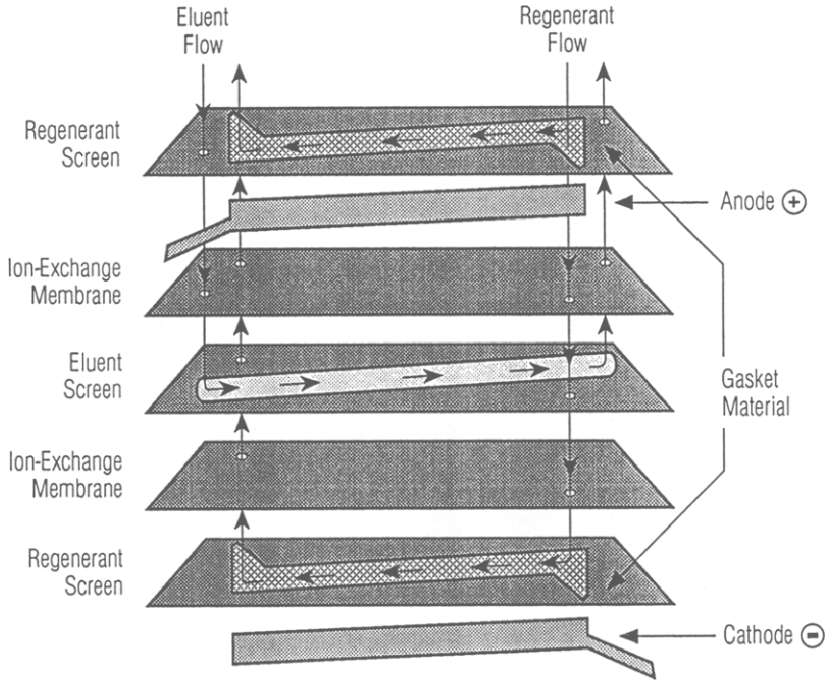

Fig. 8. Internal schematic of the Self Regenerating Suppressor.

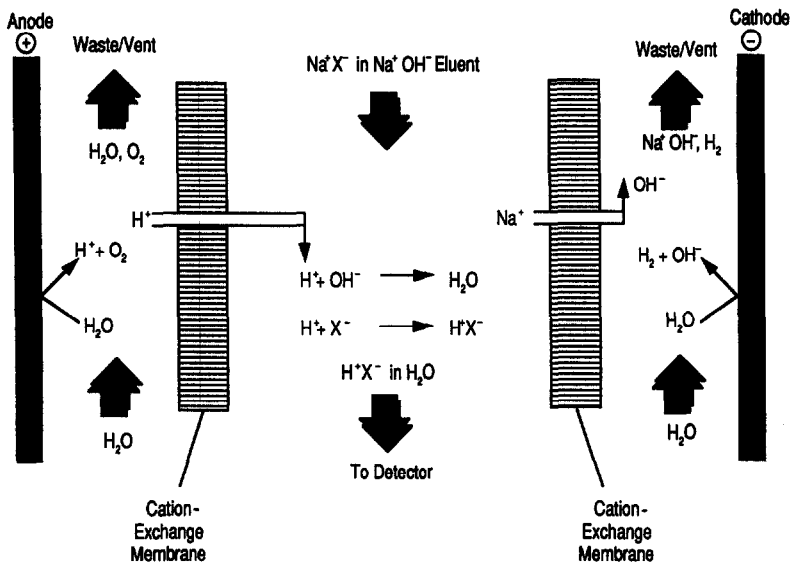

Fig. 9. Mechanism of suppression for the Anion Self Regenerating Suppressor.

traverse the cation-exchange membrane to neutralize the basic eluent, in this example, sodium hydroxide as shown in Fig. 9. The neutralized eluent proceeds to the detector cell. Sodium counterions are attracted to the negatively charged cathode, where they permeate the membrane in the cathode chamber and pair off with electrogenerated hydroxide ions to maintain electronic neutrality. Waste gases of hydrogen (from the cathode) and oxygen (from the anode) are vented with the liquid waste of aqueous sodium hydroxide. As with other suppressors, analyte signals are enhanced by exchange of their counterions with hydronium ions.

For cation analysis, the Cation Self Regenerating

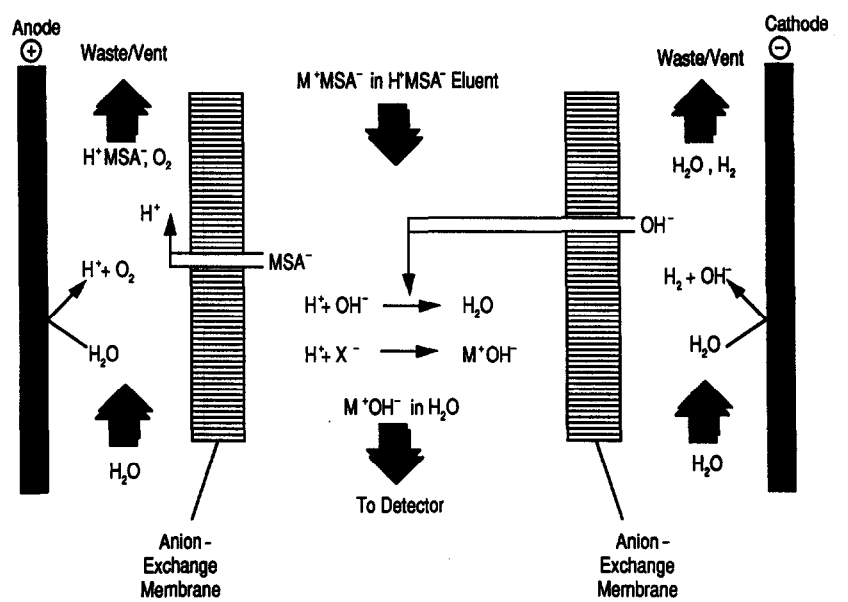

Fig. 10. Mechanism of suppression for the Cation Self Regenerating Suppressor. H^+MSA^- = Methanesulfonic acid.

Suppressor (CSRS) chemistry is shown in Fig. 10. Hydroxide ions generated at the cathode traverse the anion-exchange membrane to neutralize the acidic eluent, methanesulfonic acid in this demonstration, forming water, which continues to the detector cell. Methanesulfonate ions attracted to the anode traverse the opposing membrane, associating with hydronium ions produced at this electrode to maintain electronic neutrality. Analyte counterions are also attracted to the anode, exchanging for hydroxide ions generated at the cathode which serves to enhance the conductivity signal. As in the anion case, by-product gases and methanesulfonic acid proceed to waste and vent.

In contrast with other chemical suppressors, the SRS exhibits an overall directionality with respect to the suppression chemistry. A membrane suppressor with chemical regenerant bathing both regenerant chambers can have the regenerant ions coming from either membrane. In contrast, the ASRS generates hydronium for suppression only at the anode, so the only membrane containing and passing hydronium ions is the one in the anodic chamber. Counterion removal occurs only in the cathodic chamber and the associated membrane, where the counterion can associate with a generated hydroxide ion. The net result is that the anodic membrane is partially in the hydronium ion form, and the cathodic membrane is partially in the sodium form. CSRS chemistry is completely analogous, with one membrane in the hydroxide ion form, and the other in the methanesulfonate form.

An important concept for suppressors that use water electrolysis is the need for intimate electrical contact of the electrode with the membrane, either through direct contact or by use of an intermediate ion-exchange medium, such as functionalized screens. The electrical circuit inside the suppressor itself is conducted by ion passage through ion-exchange sites. When a regenerant ion is generated at one electrode, it sets off a cascade of ions pushing others off of ion-exchange sites until one is used for neutralization. Simultaneously, the counterion to the eluent does likewise, setting off another cascade until one leaves with the waste electrogenerated ion. The key to the function of an electrolytic suppressor is that ions have a low-resistance pathway using ion-exchange sites to flow between the electrodes to allow conductance of the electrical current.

The new suppressors have three possible operational modes. Each is designed to work for a particular set of determinations.

(1) Cell effluent recycling. The easiest operational mode utilizes the cell effluent as its deionized water source for electrolysis as shown in the schematic in Fig. 11. The eluent passes through the separation column, then proceeds to the suppressor. In the suppressor, the eluent is neutralized and the counterions removed. At this point, the suppressed eluent is largely deionized water containing a few analyte ions. This stream proceeds to the detector cell, then is routed back to the suppressor to flow through the regenerant chambers.

Recycling the cell effluent has many advantages. Beside creating a simple plumbing scheme, waste is greatly reduced. Waste volumes of an SRS-equipped IC system are now no more than that of the eluent itself while giving all of the advantages of chemical suppression. Also, there is no need for chemical regenerants such as sulfuric acid or tetrabutylammonium hydroxide as with past suppression devices. Operational costs are also greatly reduced, particularly for TBAOH which is somewhat expensive. Labor costs are also reduced as no maintenance is required.

This mode covers the vast majority of applica-

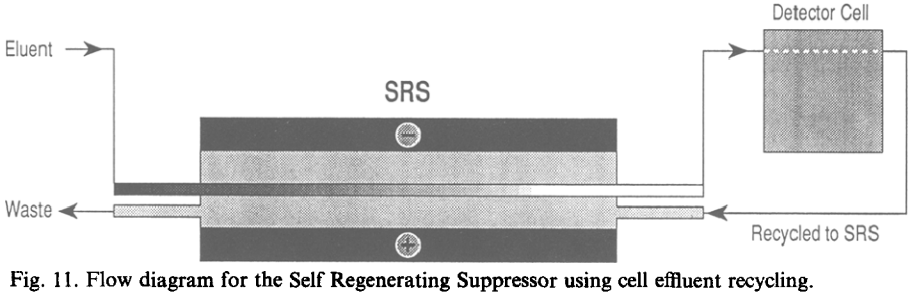

Fig. 11. Flow diagram for the Self Regenerating Suppressor using cell effluent recycling.

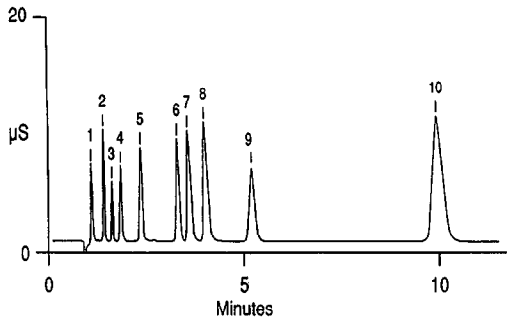

Fig. 12. Separation of common inorganic anions including oxyanions. Column: AS9-SC. Eluent: 1.8 m*M* sodium carbonate, 1.7 m*M* sodium hydrogencarbonate at 2.0 ml/min. Suppression: ASRS, cell effluent recycling. Peaks: 1 = fluoride (1 mg/l); 2 = chlorite (5 mg/l); 3 = bromate (5 mg/ml); 4 = chloride (1.5 mg/l); 5 = nitrite (6 mg/l); 6 = bromide (10 mg/l); 7 = chlorate (15 mg/l); 8 = nitrate (15 mg/l); 9 = phosphate (20 mg/l); 10 = sulfate (25 mg/l).

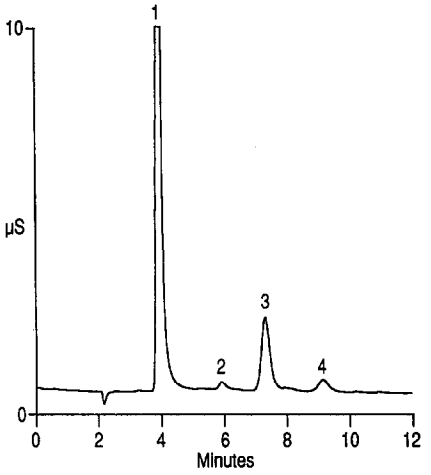

Fig. 13. Determination of cations in sea water. Column: CS12 2 mm. Eluent: 20 m*M* MSA at 0.25 ml/min. Sample diluted 1/1000, injection volume of 2.5 μl. Suppression: CSRS 2 mm, cell effluent recycling. Peaks: 1 = sodium (13.0 mg/l); 2 = potassium (0.3 mg/l); 3 = magnesium (1.2 mg/l); 4 = calcium (0.4 mg/l).

tions extant for IC today. Typical IC separations such as common inorganic anions and oxyhalides (Fig. 12) and cations in sea water on an IonPac CS12 (Fig. 13) are performed easily. Other, more difficult separations such as a steep NaOH gradient (Fig. 5) can also be done with this suppressor with a small baseline deflection.

(2) External water source. When lower system noise or higher suppression capacity is required, an external deionized water source may be used to increase the flow-rate through the regenerant chambers. This provides better sweep out of the eluent counterions, which leads to lower noise and thus more sensitivity. A pressurized bottle or pump is used to deliver water to the suppressor for the electrolytic reaction up to a flow-rate of 10 ml/min. After electrolysis, the stream containing the counterions, electrolytic side product and gases proceed to waste. The eluent stream proceeds to the detector cell as in the cell recycle model, then is also routed to waste. This mode is specialized and would only be used in a few cases.

(3) Chemical regeneration mode. The new suppressors are similar to the membrane suppressors, thus can be used with chemical regenerants as well. There are some limitations to electrolytic operation which would necessitate use of chemical regenerant.

Organic solvents, methanol in particular, are not well tolerated in the electrolytic modes. This is due to oxidation of the solvent to form ionic by-products, which create noise and high backgrounds in the chromatography. Eluents containing organic solvents can be used with chemical regenerant, such as the polyphosphoric acid run on an OmniPac PAX-100 as shown in Fig. 7.

Chloride-containing eluents also present a problem for cation determinations in the electrolytic modes. Chloride ion can oxidize to form hypochlorite which is injurious to the ion-exchange membrane. Hydrochloric acid and hydrochloride salts of amino acids are common eluents for cations. If HCl is used alone in the eluent system, however, electrolytic modes can be used by replacing the HCl with methanesulfonic acid (MSA) which is electrochemically inert. MSA is a direct replacement for HCl by using the same hydronium concentration. Samples containing chloride are not a problem since the volume injected is so small that it is highly diluted by the time it reaches the regenerant chamber and the electrode.

The new suppressors give very quiet baselines when working electrolytically, particularly when using external water as the regenerant source. When recycling the eluent as regenerant, the amount of water available is limited to the eluent flow-rate. Consequently counterion sweep out is not as facile,

TABLE I

LIMITS OF DETECTION (LOD) WITH SRS

Species	LOD, cell effluent recycle (μg/l)	LOD, external water (μg/l)
Anions[a]		
Chloride	4	2
Nitrate	12	5
Phosphate	44	17.5
Sulfate	18	8
Cations[b]		
Lithium	1	0.7
Sodium	4	2
Ammonium	5	3
Potassium	4	3
Magnesium	5	3
Calcium	8	4

[a] Conditions: column: AS4A-SC; suppressor: ASRS; eluent: 1.8 m*M* carbonate, 1.7 m*M* hydrogencarbonate; flow-rate: 2 ml/min; injection volume: 50 μl.

[b] Conditions: column: CS12; suppressor: CSRS; eluent: 20 m*M* MSA; flow-rate: 1 ml/min; injection volume: 25 μl.

leading to somewhat greater noise than when using external water, which is run typically at flow-rates at 3–10 ml/min. This does not preclude the use of recycling for most applications, however, as the increase in performance is for the most part outweighed by the convenience offered by recycling.

Detection limits (as defined as three times the baseline noise) for anions and cations by direct injection are shown in Table I. As is evident, the recycle mode gives somewhat higher detection limits than when using external water, however it is quite reasonable for most applications. Cell effluent recycling has the advantage of greater ease of use, so the somewhat elevated detection limits relative to the use of external water makes it much more desirable for routine use.

CONCLUSIONS

Suppressed IC has undergone many improvements since its early days. Suppressors have advanced from a column that required considerable user intervention to the latest, an electrolytic suppressor that is essentially invisible in operation. Analysts are always looking for greater ease of use, better performance, improved signal-to-noise ratio, and lower cost of operation. The new electrolytic suppressors described in this paper accomplish all of these while making suppression less like a post-column treatment system as has been the case in the past and more like an integral part of the overall detection scheme.

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