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# Electrochemically regenerated ion suppressors, new suppressors for ion chromatography<sup>1</sup>

Raaidah Saari-Nordhaus\*, James M. Anderson, Jr.

*Alltech Associates Inc., 2051 Waukegan Road, Deerfield, IL 60015, USA*

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## Abstract

A new electrochemically regenerated suppressor, which is based on solid-phase chemistry is described. An electrochemical process is used to regenerate the solid-phase suppressor for continuous unattended operation. Electrolysis of the detector effluent generates hydronium or hydroxide ions which automatically replace the eluent cations or anions on the suppressor. This suppressor improves and simplifies the instrumentation for suppressor-based ion chromatography. © 1997 Elsevier Science B.V.

*Keywords:* Ion suppressors; Instrumentation; Inorganic cations; Inorganic anions

## 1. Introduction

Suppressors are used in conjunction with conductivity detectors to improve detection sensitivity. The suppressor lowers the background conductance of the eluent and enhances the overall conductance of the analyte. The combination of these two factors significantly enhance sensitivity. This detection mode is used widely for the determination of anions and cations by ion chromatography (IC).

Various suppressor devices have been developed for IC. The two most common suppressors that are being used today are membrane-based suppressors [1,2] and solid-phase chemical suppressors (SPCSs) [3]. The membrane suppressor incorporates two semi-permeable ion-exchange membranes sandwiched between three sets of screens. The eluent

passes through a central chamber which has ion-exchange membrane sheets as the upper and lower surfaces. Regenerant flows in a counter-current direction over the outer surfaces of both of these membranes providing constant regeneration. The regeneration is done either by passing a constant flow of a regenerant solution from an outside source [1], or by electrolysis of water or detector effluent [2] to produce hydrogen or hydroxide ions required for regeneration. The membrane suppressors that require a constant flow of regenerant from an outside source have several drawbacks. They can consume large volumes of regenerant solution and produce large volumes of chemical waste. An additional pump or device is required to continuously pass the regenerant through the suppressor, increasing the instrument's complexity and cost while reducing reliability. The membrane-based suppressor that combines electro dialysis and electrolysis eliminates the external regenerant and associated systems. However, membrane-based suppressors can be fragile and

\*Corresponding author.

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will not tolerate much backpressure. They can rupture easily anytime as downstream backpressure increases due to blockages. Reactions that form precipitates may irreversibly damage the membranes [4]. Organic compounds present in samples may irreversibly adsorb onto the hydrophobic ion-exchange membrane reducing its efficiency to the point where it requires replacement. Membranes are typically replaced every three to twelve months depending on applications [5].

The SPCS uses disposable packed-bed cartridges as the suppression device [3]. It is more rugged than membrane-based suppressors. Since the inexpensive cartridges are discarded when exhausted, no regeneration or maintenance is required. This eliminates the need for regeneration systems or complex post-column reaction systems. Problems associated with the original packed bed suppressors such as band broadening, variable retention time and peak area and the oxidation of nitrite in the suppressor were completely eliminated [3]. Each SPCS cartridge typically provides between 6 to 16 h of operation. Fully unattended or overnight operation may not be possible for some applications.

This paper describes the use of an electrochemical process (patent pending) to regenerate the SPCS to allow continuous unattended operation. This Electrochemically Regenerated Ion Suppressor (trade mark ERIS) improves and simplifies the instrumentation required to perform suppressor-based IC.

## 2. Experimental

The ion chromatograph used was an Alltech (Deerfield, IL, USA) ion chromatography system. The Alltech Odyssey ion chromatograph consists of the Alltech Model 526 HPLC pump, ERIS 1000 autosuppressor, Model 530 column heater, and Model 550 conductivity detector. Sample introduction was performed with the Model 570 autosampler. A PE Nelson TurboChrom EL (Perkin-Elmer, San Jose, CA, USA) data station was used to record all data.

Anion separations were carried out using Alltech Allsep (100×4.6 mm), Durasep A-1 (100 mm×4.6 mm) and Anion HC (150×4.6 mm) columns. Cation

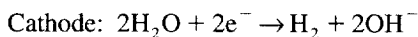
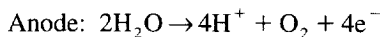
separations were carried out using an Alltech Universal Cation (100×4.6 mm) column.

Anion and cation standards were prepared by diluting the 1000 ppm certified IC standards from Alltech. Eluents were prepared using the Alltechs EZ-LUTE buffer concentrates. Deionized water was used for preparing all solutions.

## 3. Results and discussion

When an electric field is applied across two electrodes sandwiching ion-exchange resins, current is carried across the resin with low resistance. The current is believed to be carried across the resin via ion transport from one ion-exchange site to another. This discovery is used to develop the electrochemically regenerated ion suppressor (ERIS).

The ERIS Autosuppressor uses the electrolysis of water to regenerate the solid-phase suppressor cells. When water undergoes electrolysis the following reactions take place:



Hydrogen ion is produced at the anode and hydroxide ion is produced at the cathode. The detailed description of the ERIS 1000 Autosuppressor was discussed elsewhere [6]. A 10-port valve is used in the system. While one cell is used to suppress the eluent, the other cell is electrochemically regenerated. The cycling between the two electrochemical suppressor cells provides continuous instrument operation without interruption or suppressor replacement. Each suppressor cell is equipped with electrodes at each end. Fig. 1a,b show the reactions that take place during anion and cation analyses. During electrochemical regeneration of the anion cell, the hydrogen ion produced at the anode flows across the packing converting the exhausted sodium form resin back to the hydrogen form. During electrochemical regeneration of the cation cell, the hydroxide ion produced at the cathode is carried across the exhausted chloride form resin, converting it back to the original hydroxide form. No regenerant reagents or pumps are required and no chemical waste (other

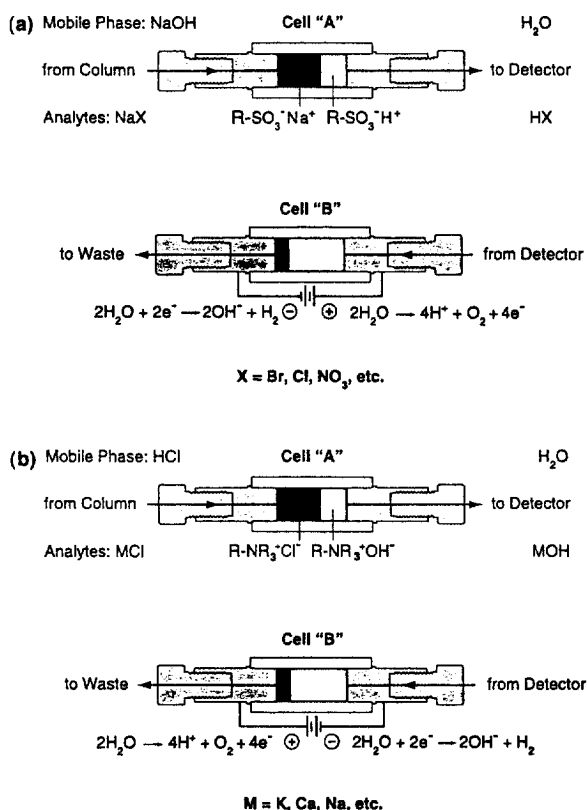


Fig. 1. Suppression and electrochemical regeneration during (a) anion analysis and (b) cation analysis. Cell 'A' suppresses the eluent while cell 'B' is electrochemically regenerated.

than the detector effluent generated on any IC system) is generated.

It was shown that the chromatographic performance of the ERIS Auto suppressor is comparable to the membrane-based suppressors [6]. The packed column suppressor introduced originally by Small et al. [7] suffered from several drawbacks such as retention time shifts, band broadening and poor peak area reproducibility for nitrate ion. These problems are eliminated with the ERIS Autosuppressor. The dimension of the ERIS suppressor cell is very small (14×7.5 mm or 7×7.5 mm), eliminating band broadening. Since the cell is always completely regenerated when an injection is made, the Donnan dialysis effect [8] is constant inside the cell and reproducible retention times are achieved. Poor reproducibility for nitrite peak area in the original suppressor was due to the conversion of nitrite to

nitrous acid and/or nitrate [9]. With the ERIS Autosuppressor to this problem is eliminated since the suppressor cell is always completely regenerated before each injection.

Because of the solid-phase chemistry the ERIS Autosuppressor offers additional advantages. It is more rugged than membrane-based suppressors and can operate at higher pressure. There is no fragile membrane to break. It is also compatible with electroactive eluents and organic containing eluents. The membrane suppressor that uses electro dialysis and electrolysis for regeneration is not compatible with electroactive eluents or eluents containing organic solvents [2]. Electroactive eluents such as hydrochloric acid, commonly employed as an eluent for cation analysis undergo electrochemical reaction in the suppressor, producing by-products that damage the membrane. These by-products will not damage the ERIS suppressor cells. Fig. 2 shows a separation of cations using hydrochloric acid as the eluent. This analysis was run continuously for two weeks and no deterioration in the suppressor cell was detected.

Organic containing eluents such as methanol,

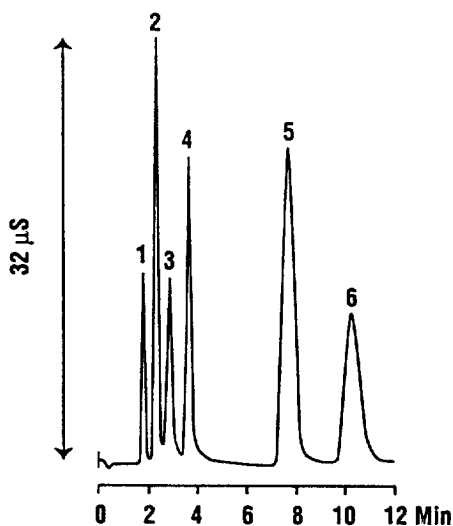


Fig. 2. Separation of cations using hydrochloric acid eluent. Peak identification: 1=lithium (0.2 ppm), 2=sodium (1.5 ppm), 3= ammonium (1.5 ppm), 4=potassium (2.5 ppm), 5=magnesium (2.0 ppm), 6=calcium (2.0 ppm). Column, universal cation (100 mm×4.6 mm); eluent, 3 mM hydrochloric acid; flow-rate, 1.0 ml/min; detection, suppressed conductivity.

undergo electrochemical reaction in the suppressor producing by-products that are conductive and interfere with the analytes detection [2]. For example, methanol is oxidized to formate and acetonitrile is oxidized to acetate during the electrolysis. Both by-products are conductive. The ERIS suppressor is compatible with organic containing eluents such as methanol and acetonitrile. These organic solvents undergo electrochemical reaction during the electrolysis, however, since the electrolysis is done on the cell that is “not active” (the cell that is off-line from the conductivity detector), the conductive by-products are eluted to waste. Fig. 3 shows a separation of anions in sea water using an eluent containing methanol.

Other separations of anions and cations using the ERIS Autosuppressor are shown in Figs. 4–6. Fig. 4 shows a separation of anions in tap water using sodium hydroxide eluent. Any element that is compatible with suppressor based IC methods can be used with

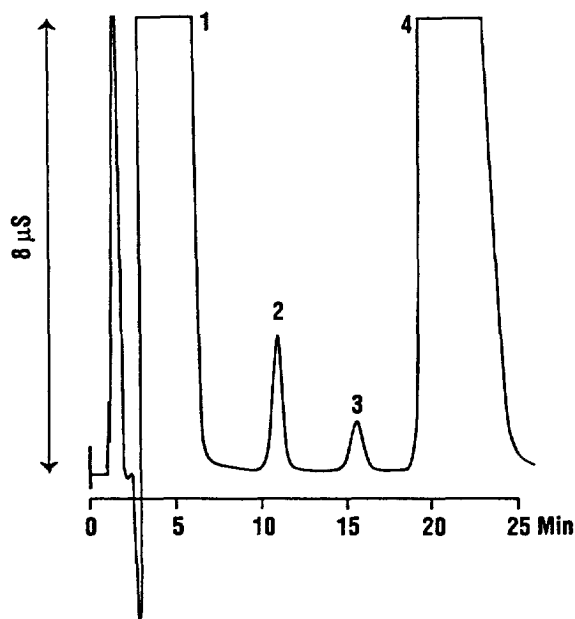


Fig. 3. Separation of anions in sea water using an eluent containing methanol. Peak identification: 1=chloride, 2=bromide, 3=nitrate, 4=sulfate. Column, anion HC (150 mm×4.6 mm); eluent, 2.8 mM NaHCO<sub>3</sub>/2.2 mM Na<sub>2</sub>CO<sub>3</sub> in 10% methanol; flow-rate, 1.4 ml/min; detection, suppressed conductivity. Injection volume: 50 μl.

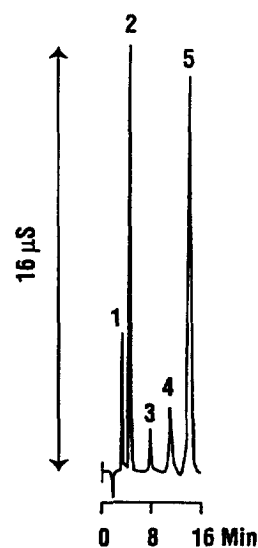


Fig. 4. Separation of anions in tap water using sodium hydroxide eluent. Peak identification: 1=fluoride, 2=chloride, 3=nitrate, 4=carbonate, 5=sulfate. Column, Allsep Anion (100 mm×4.6 mm); eluent 4 mM sodium hydroxide; flow-rate, 1.0 ml/min; detection, suppressed conductivity. Injection volume: 50 μl.

ERIS. Fig. 5 shows a separation of several anions including selenite, selenate, tungstate and molybdate using the Allsep column. Fig. 6 shows a separation of cations with sulfuric acid eluent. The hydroxide ion produced during electrolysis is capable of replacing sulfate on the suppressor.

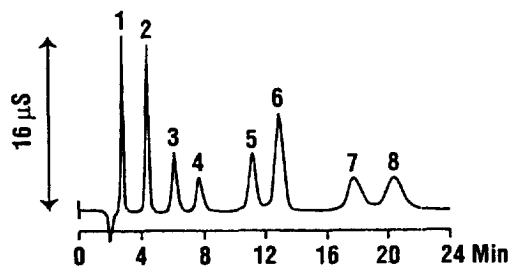


Fig. 5. Separation of anions. Peak identification: 1=fluoride, 2=chloride, 3=nitrite, 4=bromide, 5=selenite, 6=selenate, 7=tungstate, 8=molybdate. Column, Allsep Anion (100 mm×4.6 mm); eluent, 1.7 mM NaHCO<sub>3</sub>/1.8 mM Na<sub>2</sub>CO<sub>3</sub>; flow-rate, 0.8 ml/min; detection, suppressed conductivity. Injection volume: 50 μl.

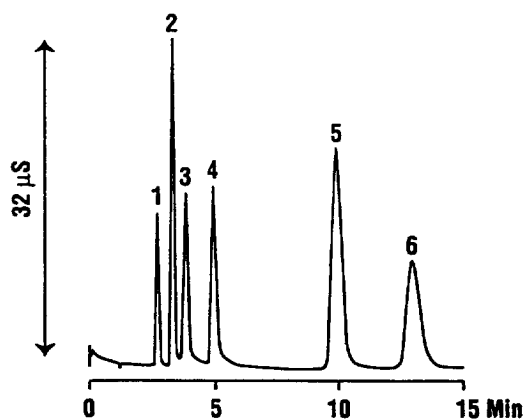


Fig. 6. Separation of cations with sulfuric acid eluent. Peak identification: 1=lithium (0.2 ppm), 2=sodium (1.8 ppm), 3=ammonium (1.5 ppm), 4=potassium (2.7 ppm), 5=magnesium (2.0 ppm), 6=calcium (2.0 ppm). Column, Universal Cation (100 mm×4.6 mm); eluent, 1.5 mM sulfuric acid; flow-rate, 1.0 ml/min; detection, suppressed conductivity. Injection volume: 50  $\mu$ l.

#### 4. Conclusion

The ERIS Autosuppressor improves and simplifies the instrumentation for suppressor-based IC. The

reliable solid-phase chemistry tolerates high back pressure, organic solvents and electroactive eluents. There are no regeneration reagents or pumps required and no chemical waste is generated. The ERIS Autosuppressor is useful in applications requiring simple, unattended operation.

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