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Review

Developments in suppressor technology for inorganic ion analysis by ion chromatography using conductivity detection

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Abstract

A review is presented detailing the development and use of suppression devices for the conductimetric detection of inorganic ions by ion chromatography (IC). An overview of the general response equation for conductivity detection is also given. Topics of discussion include the role and function of suppressors, the development of early suppressors including packed column and membrane devices from 1975 to 1990 and the subsequent progression towards present day commercially available suppressors and recent innovations. Post-suppression devices for signal enhancement are also discussed.

Keywords: Reviews; Suppressors; Ion chromatography; Conductivity detection; Inorganic ions

Contents

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1. Introduction

Since its inception in 1975 by Small et al. [1], ion chromatography (IC) has developed into a mature and highly evolved technique for the separation and determination of inorganic ions [2–4]. The most common mode of detection has been suppressed conductivity, with the function of the suppressor being to simultaneously reduce the background conductivity of the eluent prior to reaching the conductivity detector and to increase the conductivity detection signal attributable to the analyte. For example, analytes eluted from an anion-exchange column using a NaOH eluent, which is fully ionized and therefore highly conducting, results in small analyte peaks superimposed upon the high eluent background, leading to poor sensitivity and increased noise. Addition of a suppressor prior to the detector, acting as a cation-exchanger and replacing sodium counterions with hydronium ions, enables the analytes to leave the suppressor in a water solution, which is only weakly ionized thereby the background conductivity is very low. In addition, analyte response is enhanced due to the hydronium counterion being about seven times more conductive than the corresponding sodium ion. An earlier article by Jensen et al. [5] highlights the various modes of suppressed conductivity detection for IC.

Non-suppressed conductivity methods have also been extensively developed using benzoate, phthalate or other partially ionised species as mobile phases. Both suppressed and non-suppressed modes have been applied to the analysis of various complex sample matrices and indeed many IC methods have now been adopted by various international standard organizations as regulatory methods. In line with developments in IC methodology and instrumentation for conducting ions over the years, important developments have also been made in suppressor technology to increase for example their efficiency and robustness. An example is the membrane suppressor, with an historical account detailing its development since its initial conception in 1971 being given by Stevens [6], and a more detailed account of the working principles being given recently by Huang et al. [7].

This review details and discusses the developments of common forms of suppression devices fabricated over the last decade or so. Principles of conductivity detection in suppressed IC are first discussed, followed by a detailed evaluation of each type of suppressor.

2. General response equation for conductivity detection

Conductivity detection has two major advantages for inorganic ion analysis. The first is that all ions are electrically conducting, so that conductivity detection should be universal in response, and the second is that conductivity detectors are relatively simple to construct and operate. Conductivity detection is very widely employed in IC and applications are therefore abundant. A survey of the literature shows that this form of detection is employed in approximately 60% of publications dealing with IC and is utilized with ion-exchange, ion-interaction and ion-exclusion separation methods.

The operating principles of conductivity detection in IC can best be illustrated by reference to ion-exchange as the separation mode, and by considering the conductance of a typical eluent prior to and during the elution of a solute ion. For simplicity, we will consider only anion-exchange at the present time, but the detector response equations which will be developed are equally applicable to cation-exchange, provided the obvious amendments are made. Taking first the simplest case, namely that of a fully ionised eluent and analyte, it has been shown that the conductance of the background eluent, the conductance of the eluting sample band, and the measured conductance change during solute elution are given by:

$$G_{\text{Background}} = \frac{(\lambda_{E^+} + \lambda_{E^-})\, C_E}{10^{-3}\, K} \tag{1}$$

$$G_{\text{Elution}} = \frac{(\lambda_{E^+} + \lambda_{E^-})(C_E - C_S)}{10^{-3}\, K} + \frac{(\lambda_{E^+} + \lambda_{S^-})\, C_S}{10^{-3}\, K} \tag{2}$$

$$\Delta G = G_{\text{Elution}} - G_{\text{Background}} = \frac{(\lambda_{S^-} - \lambda_{E^-})\, C_S}{10^{-3}\, K} \tag{3}$$

Here, the eluent comprises the electrolyte E^+E^- and the analyte anion is represented by S^-. G_{Elution} is the

conductance of the analyte band, $G_{Background}$ is the conductance of the background, and ΔG is the change in conductance during elution of the analyte. λ_{S^-}, λ_{E^+} and λ_{E^-} are the limiting ionic conductances of the analyte ion and eluent ions, respectively, C_S and C_E are the total concentrations of the analyte and eluent ions (i.e. their ''formal'' concentration), and K is the conductivity cell constant, expressed in cm^{-1}. Eqs. (1)–(3) enable conductance changes to be calculated under various conditions, provided that values for limiting equivalent ionic conductances are known. Tables 1 and 2 list values for some common ions and represent a compilation of data taken from numerous literature sources.

Considering now the case where both the eluent and the analyte are not completely dissociated as a result of the operating pH of the eluent system, it is convenient to define I_E as the fraction of the total eluent concentration (C_E) that is dissociated. Similarly, we can define I_S as the fraction of the total analyte concentration (C_S) that is dissociated (note that I is equivalent to α, which is a commonly used term to denote the fraction of a species existing in a particular form). The following assumptions are made:

(i) The analyte binds to the resin only as S^-.
(ii) Even when analyte is injected as a mixture of its protonated (HS) and deprotonated (S^-) forms, all of the analyte becomes bound to the stationary phase as S^-. However, it should be re-

Table 1
Limiting equivalent ionic conductances of some anions in aqueous solution

Anion	λ_- (S cm^2 $equiv^{-1}$)	Anion	λ_- (S cm^2 $equiv^{-1}$)
OH^-	198	$DTPA^{3-}$	46
$Fe(CN)_6^{4-}$	111	$Trimellitate^{3-}$	46
$Fe(CN)_6^{3-}$	101	HCO_3^-	45
CrO_4^{2-}	85	$Succinate^{2-}$	43
CN^-	82	$Acetate^-$	41
SO_4^{2-}	80	$2,6\text{-}Pyridinedicarboxylate^{2-}$	40
Br^-	78	$Phthalate^{2-}$	38
I^-	77	$Propionate^-$	36
Cl^-	76	Salicylate	36
$P_2O_7^{4-}$	75	$Pyruvate^-$	35
$C_2O_4^{2-}$	74	$Butyrate^-$	33
CO_3^{2-}	72	$Benzoate^-$	32
MoO_4^{2-}	72	$2,3\text{-}Dihydroxybenzoate^-$	32
NO_3^-	71	$2\text{-}Naphthalenesulfonate^-$	32
PO_4^{3-}	69	$Picrate^-$	30
ClO_4^-	67	$Nicotinoate^-$	33
SCN^-	66	$Hexanoate^-$	29
ClO_3^-	65	$Phenylacetate^-$	29
$S_4O_6^{2-}$	63	$Pentanesulfonate^-$	29
$P_3O_{10}^{5-}$	63	$Anisate^-$	29
$1,3,6\text{-}NTS^{3-}$	60	$p\text{-}Aminosalicylate^-$	29
Malonate	59	$p\text{-}Aminobenzoate^-$	28
$Citrate^{3-}$	56	$Lactate^-$	28
$Formate^-$	55	$Hexanesulfonate^-$	27
F^-	54	$Sorbate^-$	27
$1,3\text{-}Benzenedisulfonate^{2-}$	53	$Octanesulfonate^-$	24
$Pyromellitate^{4-}$	53	$Valerate^-$	24
NTA^{3-}	50	$Heptanoate^-$	21
$EDTA^{3-}$	48	$Octanoate^-$	20
$Malate^{2-}$	48	$Laurate^-$	9
$1,5\text{-}NDS^{2-}$	46		

NTS = naphthalenetrisulfonate; NDS = naphthalenedisulfonate; NTA = nitrilotriacetate; EDTA = ethylenediaminetetraacetate; DTPA = diethylenetriaminepentaacetate.

Table 2
Limiting equivalent ionic conductances of some cations in aqueous solution

Cation	λ_- (S cm^2 equiv^{-1})	Cation	λ_- (S cm^2 equiv^{-1})
H_3O^+	350	Na^+	50
Rb^+	78	Dimethylamine$^+$	49
Cs^+	77	4-Aminopyridine$^+$	46
K^+	74	Ethanolamine$^+$	43
NH_4^+	73	$N(CH_3)_4^+$	42
Pb^{2+}	71	Phenylethylamine$^+$	40
Ce^{3+}	70	Li^+	39
Fe^{3+}	68	Benzylamine$^+$	38
Cr^{3+}	67	Propylamine$^+$	38
Ba^{2+}	64	Pyridine$^+$	37
Al^{3+}	61	4-Methyl-2-benzylamine$^+$	35
Ca^{2+}	60	Diethylamine$^+$	35
Sr^{2+}	59	Morpholine$^+$	33
Imidazole$^+$	59	$N(C_2H_5)_4^+$	33
Methylamine$^+$	58	Diethanolamine$^+$	32
Cu^{2+}	55	Benzylamine$^+$	32
Cd^{2+}	54	Butylamine$^+$	32
Fe^{2+}	54	Phenyltrimethylamine$^+$	30
Mn^{2+}	54	Methylpyridine$^+$	30
Mg^{2+}	53	Histidine$^+$	29
Co^{2+}	53	$N(C_3H_7)_4^+$	23
Zn^{2+}	53	Methyl Green$^+$	22
Ni^{2+}	50		

membered that most of the analytes used in IC are anions of strong acids and therefore are normally present only in the fully ionised form.

(iii) Both the protonated (HE) and deprotonated (E^-) forms of the eluent participate in the elution process.

The conductance change accompanying elution of the sample is given by:

$$\Delta G = G_{\text{Elution}} - G_{\text{Background}} = \left(\frac{(\lambda_{E^+} - \lambda_{S^-})\, I_S - (\lambda_{E^+} + \lambda_{E^-})\, I_E I_S}{10^{-3} K} \right) C_S \qquad (4)$$

A number of important observations arise from Eq. (4). First, the conductance signal is proportional to the analyte concentration, C_S, and increases as the degree of ionization of the analyte in the eluent phase, I_S, is increased. Second, the conductance change predicted by Eq. (4) is zero when the eluent and the analyte are the same. Third, Eq. (4) shows that in non-suppressed IC the detection signal increases as I_E decreases, so that eluents which are weakly dissociated give more sensitive detection than those that are strongly dissociated. This has been demonstrated by Gjerde and Fritz [8] who showed that benzoic acid eluents gave more sensitive detection than potassium benzoate eluents. The reason for this is that the undissociated eluents contribute a H^+ ion to the analyte band for each eluent molecule involved in the elution. The H^+ ions formed in this way are highly conducting and enhance the detection signal. This mechanism of signal enhancement is identical to that used in suppressed IC (see Section 4). Finally, when a fully ionised eluent and analyte are used (i.e. I_E and I_S are unity), Eq. (4) simplifies to Eq. (3).

3. General discussion of suppressors

3.1. Purpose and functioning of suppressors

The magnitude of the conductance change accompanying elution of a particular analyte by a specified eluent can be calculated from Eq. (4). To illustrate this process, we can envisage the situation where a

10 mg l^{-1} Cl^- solution is injected and that a fivefold dilution of the sample occurs during passage of the solute through the chromatographic column, so that the concentration of Cl^- in the detection cell is 2 mg l^{-1} (5.63×10^{-5} *M*). Assuming a cell constant of 10 cm^{-1} for the conductivity detector, then the conductance change on sample elution can be calculated for three different eluents, namely 1 m*M* potassium benzoate, 1 m*M* sodium bicarbonate, and 1 m*M* sodium hydroxide. The calculated conductance change for each eluent is listed in Table 3, together with the background conductance of the eluent calculated from Eq. (1). The benzoate eluent gives a modest conductance change, the carbonate eluent gives a lower response, whilst the hydroxide eluent gives an appreciable, but negative, conductance change. The benzoate eluent is therefore suitable for direct conductivity detection (and this type of response forms the basis of non-suppressed conductivity detection), the hydroxide eluent is suitable for indirect conductivity detection (and hydroxide is also used in non-suppressed IC), whilst the bicarbonate eluent gives the lowest response.

Conductivity detection using hydroxide or bicarbonate eluents (used alone or in combination with carbonate) can be improved greatly by exchanging hydrogen ions for the cations in the eluent, prior to the measurement of conductance. The hydroxide ions are converted to water and bicarbonate (and carbonate) ions are converted into weakly conducting carbonic acid. The background conductance of the eluent is said to be *suppressed*, as shown in Table 3.

The most simple means of accomplishing eluent suppression is to pass the eluent through a cation-exchange column in the hydrogen form. To illustrate the reactions which take place in such a suppressor column, consider the case of chloride ions as solute and an eluent composed of sodium bicarbonate. The eluent reaction in the suppressor is given by Eq. (5), whilst the reaction of the solute is given by Eq. (6):

$$\text{Resin–H}^+ + \text{Na}^+\text{HCO}_3^- \rightleftharpoons \text{Resin–Na}^+ + \text{H}_2\text{CO}_3 \quad (5)$$

$$\text{Resin–H}^+ + \text{Na}^+ + \text{Cl}^- \rightleftharpoons \text{Resin–Na}^+ + \text{H}^+ + \text{Cl}^- \quad (6)$$

The combined result of these processes is that the eluent conductance is decreased greatly, whilst the conductance of the sample is increased by virtue of the replacement of sodium ions ($\lambda_+ = 50$ S cm^2 $equiv^{-1}$) with hydrogen ions ($\lambda_+ = 350$ S cm^2 $equiv^{-1}$). The detectability of the solute is therefore enhanced, as indicated in Table 3. A similar procedure can be applied to cation-exchange, where the suppressor is now an anion-exchange column in the OH^- form and operates by the addition of OH^- ions to the eluent.

Suppression reactions are not limited to acid–base reactions, such as those shown in the above examples. Indeed, any post-column reaction which results in a reduction of the background conductance of the eluent can be classified as a suppression reaction. Examples of such reactions would include complexation and precipitation reactions, but the ensuing discussion of suppressor design and performance will

Table 3
Conductance change on elution of 10 mg l^{-1} chloride with various eluents

Eluent	Suppression	Background conductance (μS)[b]	Conductance change (ΔG) (μS)	Detection mode
1 m*M* KBz[a]	No	10.6	0.25[c]	Direct
1 m*M* NaOH	No	24.8	−0.86[c]	Indirect
1 m*M* $NaHCO_3$	No	9.5	0.18[c]	Direct
1 m*M* NaOH	Yes	0	2.4[d]	Direct (suppressed)
1 m*M* $NaHCO_3$	Yes	0.4	2.4[d]	Direct (suppressed)

[a] Bz = benzoate anion.
[b] Calculated from Eq. (1).
[c] Calculated from Eq. (3).
[d] Calculated from Eq. (9).

be restricted to those which employ acid–base reactions, since these are the most widely used.

3.2. Response equation for suppressed conductivity detection

A response equation for conductivity detection in suppressed IC systems can be derived for an anion-exchange system in which the eluent consists of an ionic salt, NaA, present at concentration C_E. A fully ionized sample anion, S^-, is eluted from the column at a concentration of C_S. This solute is accompanied by an equivalent concentration of H^+ as a result of the suppression reaction.

For suppression to be effective, the eluent anion, A^-, must be the conjugate of a weak acid, HA. Passage of the eluent through the suppressor results in the formation of HA, which ionizes according to:

$$K_{HA} = \frac{[H^+][A^-]}{[HA]} \quad (7)$$

When the eluent is converted fully to HA in the suppressor, the conductance of the suppressed eluent and the suppressed sample results from H^+, A^- and S^- ions. However, when the suppression reaction is not quantitative (i.e. not *all* of the Na^+ ions from the eluent are removed), we can expect the suppressed eluent to contain some residual Na^+ ions which will also contribute to the conductance. As mentioned in the introduction, incomplete suppression of the eluent counterion will result in an increase in background noise and a subsequent decrease in analyte sensitivity. Finally, we must consider any OH^- which may be present in the suppressed eluent.

By treating the appropriate equilibria we can derive that the conductance measured during sample elution is given by:

$$G_{Sample} = \frac{(\lambda_{H^+}[H^+] + \lambda_{OH^-}[OH^-] + \lambda_{Na^+}[Na^+] + \lambda_{S^-}[S^-] + \lambda_{A^-}[A^-])}{10^{-3}K} \quad (8)$$

In the ideal case, the suppression reaction will be quantitative (i.e. $[Na^+]=0$) and the product of the suppressor reaction (HA) will not dissociate to any appreciable extent (i.e. $[A^-]=0$). Under these conditions, the detector signal arises entirely from S^- and an equivalent amount of H^+. That is:

$$G_{Ideal} = \frac{(\lambda_{H^+} + \lambda_{S^-})\,C_S}{10^{-3}K} \quad (9)$$

Eq. (9) was used to calculate the detector responses for the suppressed eluents shown in Table 3.

4. Early suppressors (1975–1990)

4.1. Packed-column suppressors

The first suppressor [1] was an ion-exchange column in the H^+ or OH^- form, which operated according to the mechanism discussed above. High capacity ion-exchange materials were used in order to provide the greatest possible reservoir of H^+ or OH^- ions and to enable the suppressor to be used for as long a time as possible. However, it was still necessary for the suppressor to be regenerated periodically off-line by passing an appropriate solution (such as 0.25 N H_2SO_4 for the H^+ form suppressor) through the column to displace the accumulated eluent cations.

Packed-column suppressors suffered from a number of disadvantages which included the need for off-line regeneration, band-broadening occurring in the suppressor, resulting in loss of chromatographic efficiency, and some solute ions which could be protonated easily showed variable retention in the suppressor column due to ion-exclusion effects. Despite these disadvantages, packed column suppressors provided the foundation on which the technique of IC was built and were in use from 1975 to 1981. It is noteworthy that there has been a recent resurgence in the use of column suppressors, as discussed later, and it is a most unusual occurrence in analytical chemistry for technology which is more than 25 years old to be reintroduced.

4.2. Hollow-fibre membrane suppressors

Hollow fibres constructed from polymeric ion-exchange material provided an alternative means for eluent suppression. The eluent is passed through the lumen of the fibre, whilst a suitable regenerant (or

scavenger) solution passes over the exterior of the fibre, usually in a countercurrent direction. The first hollow-fibre suppressor was reported by Stevens et al. [9] and consisted of a collection of sulfonated cation-exchange fibres, with which sulfuric acid was used as the regenerant. The mode of operation of this suppressor with a bicarbonate/carbonate eluent is illustrated schematically in Fig. 1. The overall results of these processes are identical to those achieved by the column suppressor, but the hollow-fibre design had the chief advantages of greatly reduced band-broadening and continuous regeneration [10,11]. It has also been noted that suppression efficiency is increased at elevated temperatures because of improved diffusion of ions both in solution and through the membrane [10,12].

Transfer of ions through the fibre was found to be enhanced if some type of inert packing was inserted into the fibre. Typical packings were nylon filaments or polystyrene beads and these served to also decrease the dead volume inside the suppressor. Such packed-fibre suppressors were developed extensively using such approaches as replacing the inert beads with ion-exchange resin beads, packing beads around the exterior of the fibre to provide mechanical support, altering the shape of the packing beads and application of an ultrasonic field to the system. The effects of these approaches have been discussed in some detail by Dasgupta [13].

The regenerant employed with fibre suppressors must supply the ion required for effective eluent suppression (e.g. H^+ or OH^-), but must not contaminate the eluent with any other ion. The chief potential contaminant is the regenerant ion having the *same* charge sign as that of the solute. Whilst this ion is theoretically prevented from entering the eluent stream as a result of Donnan exclusion by the ion-exchange functionality on the fibre, this repulsive effect may not totally prevent penetration of the forbidden ion, especially when the regenerant concentration is high. For this reason it was common to use regenerants containing large co-ions, such as dodecylbenzenesulfonate.

4.3. Micromembrane suppressor

The chief drawback of fibre suppressors was that the small internal diameter of the fibre meant that the surface area of the fibre was low, and this, in turn, led to low ion-exchange and thereby low suppression

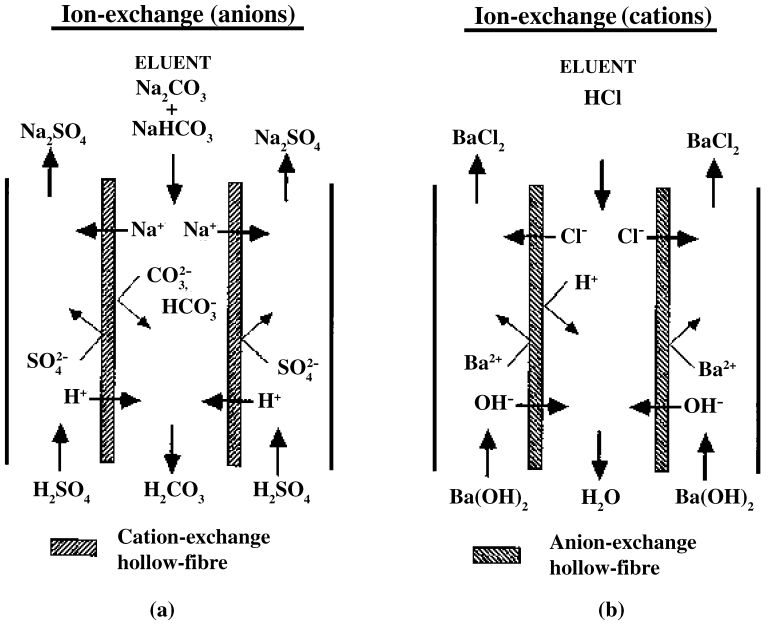

Fig. 1. Schematic operation of a hollow fibre suppressor for (a) anion-exchange and (b) cation-exchange separations.

capacity. The eluent concentrations suitable for use with such a suppressor were therefore restricted. In addition, there were some mechanical problems in connecting the fibres to the eluent flow and the fibres were intolerant towards some organic solvents.

These problems were overcome by introduction of the micromembrane suppressor, in which the fibre was replaced with flat sheets of membrane [14]. The surface area available for exchange between eluent and regenerant ions and the ion-exchange capacity were increased greatly. The design of a micromembrane suppressor is shown schematically in Fig. 2.

Eluent is passed through a central chamber which has ion-exchange membrane sheets as the upper and lower surfaces. Regenerant flows in a countercurrent direction over the outer surfaces of both of these membranes. Mesh screens constructed from a polymeric ion-exchange material are inserted into the eluent cavity and also into the cavities which house the flowing regenerant solution. The entire device is constructed in a sandwich layer configuration with gaskets being used to define the desired flow-paths. The volume of the eluent chamber is very small, <50 μl [14], so band-broadening is minimal.

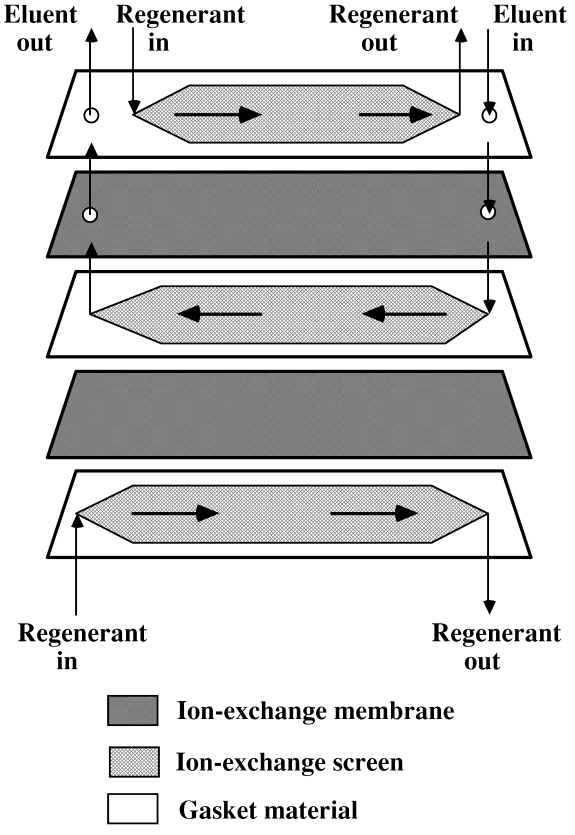

Fig. 2. Design of a micromembrane suppressor. Adapted from Ref. [14].

The micromembrane suppressor operates on the same principles as the fibre suppressors, but high-capacity ion-exchange screens are used to bring eluent and sample ions to the membrane surface in order to facilitate transfer with regenerant ions. This mechanism of ion transport plays an increasingly important role as the eluent passes from the suppressor inlet towards the outlet. During this passage, the suppressor reaction advances towards completion and there are relatively fewer eluent ions remaining to react, so effective transport is essential. The *dynamic suppression capacity* (i.e. the number of microequivalents of eluent which can be suppressed per unit time) increases with increasing ion-exchange capacity of the screen material [14] and also increases with the concentration of the regenerant solution. When 12.5 m*M* sulfuric acid was used as regenerant at a flow-rate of 10 ml min^{-1}, the dynamic capacity of the micromembrane suppressor exceeded 100 μequiv min^{-1} [14,15]. This means that an eluent of 100 m*M* NaOH, flowing at 1 ml min^{-1} (i.e. 100 μequiv ml^{-1}), could be suppressed effectively.

The advantages of the micromembrane suppressor included minimal band-broadening effects, continuous regeneration, high dynamic suppression capacity, suitability for gradient elution, and resistance to many organic solvents. Perhaps the one major drawback of the micromembrane suppressor was that it required a constant supply of regenerant, typically delivered pneumatically at flow-rates up to 10 ml min^{-1} for optimal performance. This process consumed large volumes of regenerant, necessitating large reservoirs of the chemicals needed for suppression [16]. One solution to this problem was to continuously recycle the regenerant through a high capacity ion-exchange cartridge. The ‘‘AutoRegen’’ device, introduced in 1987, used a pump to recirculate the regenerant through the suppressor and cartridge [16]. In the case of anion analysis, the suppression product for a sulfuric acid regenerant is sodium hydrogensulfate. When passed through a

cation-exchanger in the hydronium form, this solution is converted back to sulfuric acid, thus ensuring a fresh supply of regenerant solution for the suppression reaction. This device enabled the suppressor to be operated for about 30 days without any interruption when using typical conditions for anion analysis [2].

A less complex means of extending the operation of the micromembrane suppressor has recently been suggested. This mode of operation, termed ''displaced chemical regeneration'' involves directing the effluent from the conductivity cell into a sealed bottle filled with regenerant [17]. A sulfuric acid regenerant, which has a higher density than the suppressed eluent (essentially water), is displaced from the bottom of the sealed bottle, at the same flow-rate used for the analytical separation, and passes through the regenerant chambers of the micromembrane suppressor, as shown in Fig. 3. As long as the sealed bottle contains no headspace air and is filled with an appreciable volume of regenerant at an appropriate concentration, the suppression reaction can continue to occur until the regenerant becomes too dilute to maintain sufficient flux of the regenerant ion.

One disadvantage of this approach is that the regenerant is delivered at a much lower flow-rate than used normally, so the concentration of regenerant needs to be correspondingly higher than the 10–25 m*M* sulfuric acid which was used typically [16]. A consequence of using the higher regenerant concentration is that greater penetration of the forbidden ion across the suppressor membranes occurs, leading to a higher background conductance of the suppressed eluent. For example, when using an eluent of 9.0 m*M* sodium carbonate operated at a flow-rate of 1.0 ml min^{-1}, the background conductance after suppression using a regenerant of 75 m*M* sulfuric acid in displaced chemical regeneration mode is 24 μS, as opposed to 22 μS when the same eluent was operated in the conventional manner. The advantage of the displaced chemical regeneration mode is that 2.0 l of 75 m*M* sulfuric acid regenerant could continuously suppress a 9.0 m*M* sodium carbonate eluent for more than 24 h before any loss of system performance is observed [17].

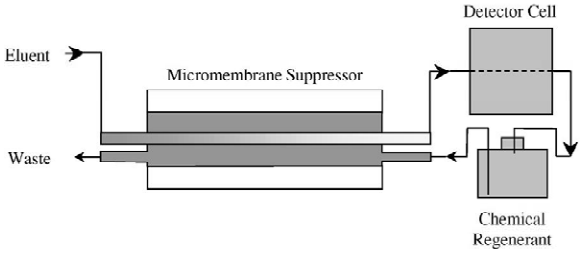

Fig. 3. Displaced chemical regeneration mode of operation for a micromembrane suppressor.

5. Modern suppressors (1990–present)

5.1. Electrolytic membrane-based suppressors

The use of membrane-based suppressors in which transfer of ions across the membrane is enhanced with an electric field was suggested by Tian et al. [18] as a more efficient design in comparison to those suppressors in which ion transport is accomplished by diffusion alone. Several variations of this concept were developed in the late 1980s, based upon both flat sheet [18] and tubular membranes [19] and a commercially available electrolytic suppressor was introduced in 1992 [16]. This suppressor incorporated electrolysis reactions of water to generate the hydronium ions necessary for the suppression reaction. A flat membrane design similar to that of the micromembrane suppressor was used, with two electrodes incorporated into the design to allow electrolysis of water to occur. This device was termed the ''Self Regenerating Suppressor'' or SRS, as no external regenerant was required in order to achieve the suppression reaction [20].

The internal design of a self regenerating suppressor is shown in Fig. 4. Functionalized ion-exchange screens are present in the regenerant chambers to facilitate the passage of electric current, with ion-exchange membranes being used to define an eluent chamber containing an ion-exchange screen, similar to the design of the micromembrane suppressor. The two platinum electrodes are placed in the regenerant chambers between the regenerant screens and the outer hardware shell. A constant current power supply generates the electric field for the electrolytic reaction. Because this design allows the use of very low flow-rates for the water used as the basis of the

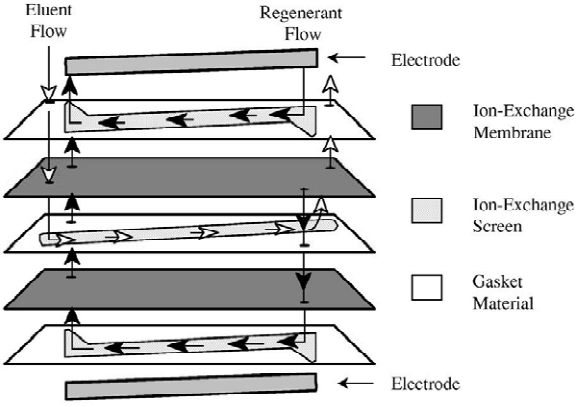

Fig. 4. Design of an electrolytic membrane-based suppressor. Adapted from Ref. [16].

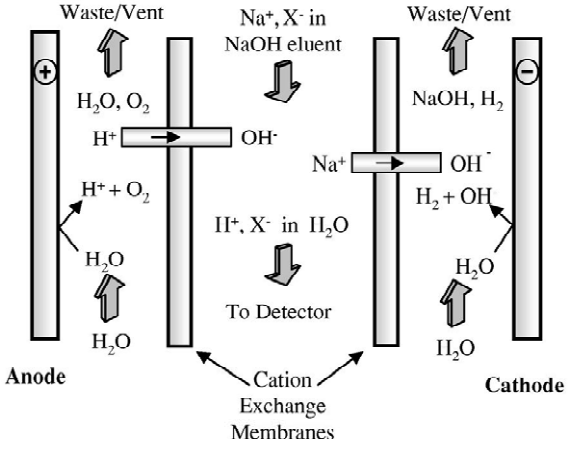

Fig. 5. Mechanism of suppression for the anion SRS. Adapted from Ref. [16].

electrolysis reaction, the device can use the deionized eluent (produced after the suppression reaction) from the detector cell as its water source. Alternatively, an external source of water can be used. Since the electrolysis of water is the source of the regenerant ions, no independent chemical feed solution is required, as was the case for previous designs of continuously regenerated membrane-based suppressors.

The neutralization reactions occurring in the SRS are essentially the same as those of other membrane-based suppressors. For anion analysis using an Anion SRS, hydronium ions generated at the anode migrate across the cation-exchange membrane to neutralize the basic eluent, in this example, sodium hydroxide, as shown in Fig. 5. The neutralized eluent then proceeds to the detector cell. Sodium counter-cations from the eluent are driven toward the negatively charged cathode, and migrate across the cation-exchange membrane where they then pair with hydroxide ions, thus maintaining electroneutrality. Waste gases of hydrogen (from the anode) and oxygen (from the cathode) are vented out of the regenerant chambers with the liquid waste of sodium hydroxide.

For cation analysis using a cation SRS, hydroxide ions generated at the cathode migrate across the anion-exchange membrane to neutralize the acidic eluent. This process can be exemplified using methanesulfonic acid (MSAH) as the eluent. MSA^- counter-anions from the eluent are attracted to the positively charged anode, before migrating across the anion-exchange membrane and pairing with hydronium ions to maintain electroneutrality. The neutralized eluent proceeds to the detector cell, while waste gases are vented out of the regenerant chambers along with the liquid waste.

The SRS can be operated in a number of ways. The most straightforward mode of operation is to use the effluent from the conductivity detector cell as the source of deionized water required for electrolysis, as shown in Fig. 6. This is called ''recycle mode'' and this form of operation of the SRS greatly simplifies the plumbing scheme of the IC instrument. There is no longer any need for a chemical regenerant and waste volumes and operational complexity are also reduced. This mode of operation covers the majority of routine IC applications which utilize suppressed conductivity detection [16].

The SRS can also be operated in the ''external water mode'' where an external source of deionized

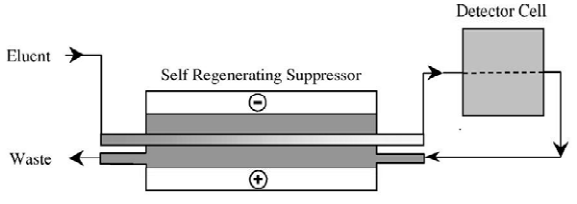

Fig. 6. Recycle mode of operation for an SRS. Adapted from Ref. [16].

water is supplied, at an increased flow-rate, through the regenerant chambers while the cell effluent is directed to waste. The higher flow-rate leads to faster sweep out of the eluent counter-ions and electrolysis products, which leads to lower noise and hence improved sensitivity. This mode of operation also increases the dynamic suppression capacity of the SRS. The deionized water is supplied from a pneumatic reservoir at flow-rates of up to 10 ml min^{-1}, in essentially the same manner that the chemical regenerant is conventionally delivered to a micromembrane suppressor. This mode of operation is recommended for suppressed conductivity applications where maximum sensitivity is required, such as the determination of low $\mu g\ l^{-1}$ levels of disinfection by-product anions or perchlorate in drinking waters [21,22]. Table 4 shows a comparison of the limits of detection obtained using an electrolytic SRS operated using recycle and external water modes [16].

Apart from the addition of platinum electrodes and some minor differences in the materials of construction, the SRS devices are similar to conventional micromembrane suppressors and can therefore also be used with chemical regenerants. There are some limitations to electrolytic operation which necessitate the use of chemical regeneration mode under some circumstances. Organic solvents, such as methanol and acetonitrile, can permeate the ion-exchange membranes and become oxidized at the electrode surfaces to form ionic by-products. This increases background conductance and creates additional baseline noise, so it is preferable that the chemical regeneration mode be used with an SRS device for eluents containing high levels of organic solvents [16].

Table 4
SRS limits of detection in recycle and external water modes [16]

Solute		LOD[a], recycle mode ($\mu g\ l^{-1}$)	LOD, external mode ($\mu g\ l^{-1}$)
Anions[b]	Chloride	4	2
	Nitrate	12	5
	Phosphate	44	18
	Sulfate	18	8
Cations[c]	Lithium	1	0.7
	Sodium	4	2
	Ammonium	5	3
	Potassium	4	3
	Magnesium	5	3
	Calcium	8	4

[a] LOD = limit of detection, determined as three times signal-to-noise.

[b] Conditions: column: AS4A-SC; suppressor: ASRS; eluent: 1.8 m*M* carbonate–1.7 m*M* hydrogen-carbonate; flow-rate: 2.0 ml min^{-1}; injection volume: 50 μl.

[c] Conditions: column: CS12; suppressor: CSRS; eluent: 20 m*M* methanesulfonic acid; flow-rate: 1.0 ml min^{-1}; injection volume: 25 μl.

Eluents containing oxidisable ionic species, such as chloride or *p*-cyanophenol, also present a problem when using the SRS in the electrolytic mode. Hydrochloric acid and hydrochloride salts of amino acids are common eluents for cation separations. Chloride can be oxidised to form hypochlorite, which damages the ion-exchange membranes and reduces the performance of the SRS. Chemical regeneration mode is therefore recommended for use with eluents containing chloride or *p*-cyanophenol.

While the various modes of operation allow self regenerating suppressors to be employed for a very wide range of applications in IC, recycle mode is by far the most commonly used as it greatly simplifies operation of the IC instrument. The drawback of this approach is that maximum sensitivity is not achieved because the eluent counter-ions and electrolysis products are only removed from the device at the flow-rate dictated by the analytical separation. A variation on this electrolytic mode of operation has recently been described in which an inert gas, flowing at 100 ml min^{-1}, is used to supplement the effluent flow from the detector cell, as shown in Fig. 7 [17]. The use of ''gas assisted recycle mode'' allows rapid removal of the eluent counter-ions and electrolysis products, and provides a similar level of performance to the external water mode, but with less complexity and the reduced reagent consumption of the recycle mode. In fact, this mode of operation has been shown to reduce baseline noise for anion analysis by a factor of two compared even to the external water mode, as a result of more rapid removal of electrolysis gases [17].

5.2. Packed-column mini-suppressors

Despite the disadvantages discussed earlier, almost all the early applications of IC utilized packed-

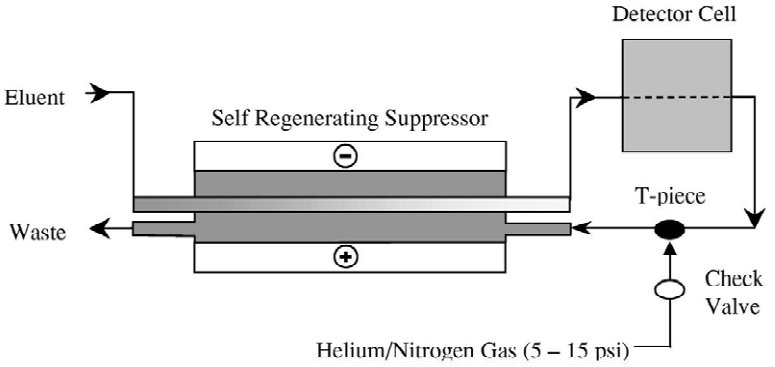

Fig. 7. Gas-assisted recycle mode of operation for an SRS.

column suppressors. The developments in 1979 by Fritz et al. [23], which showed that a suppressor was not essential for conductivity detection, and the introduction of membrane-based suppressors shortly after in 1981 [9], created little technical need for continued use of packed-column suppressors. However, the expiration of the patent describing the original packed-bed suppressor revived commercial interest in the use of this approach, as it enabled instrument companies other than Dionex to offer the option of suppressed conductivity detection, for example the Lachat Instruments Quikchem suppressor cartridge for anion analysis [24].

The first commercially available implementation of this approach, termed ''Solid Phase Chemical Suppression'', devised by associates at Alltech Inc., used a unique valve configuration with two disposable suppressor cartridges [25], as shown in Fig. 8.

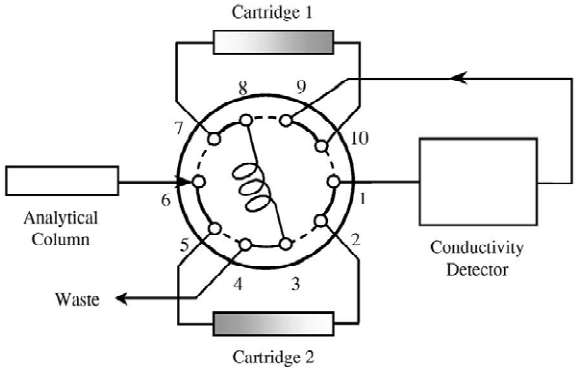

Fig. 8. Valve configuration for Solid Phase Chemical Suppression. Adapted from Ref. [25].

Each cartridge provides continuous suppression for a relatively short period of time, between 7 and 12 h for anion analysis and 4–6 h for cation analysis. The transparent cartridges have a pH indicator adsorbed onto the ion-exchange resin which, in the case of anion analysis, changes from gold to magenta as the cartridge is converted from the hydronium to the sodium form. As one cartridge approaches exhaustion, the user manually switches the 10-port valve and directs the eluent toward the fresh cartridge, thus maintaining continuous suppression. The spent cartridge can then be replaced with a new cartridge to perpetuate the cycle. A similar approach using methyl yellow indicator adsorbed onto Dowex 50W-X8 cation-exchange resin has been also been reported [26]. The resin is packed into a small glass column, allowing the user to visually monitor the degree of exhaustion of the suppressor. The packed-column suppressor can be regenerated off-line and then re-used since the indicator remains adsorbed on the suppressor column during regeneration.

The approach described above suffers from some practical limitations because periodic manual intervention is required to maintain the suppression reaction. Hence, it offered no significant *technical* benefit over the original packed bed suppressor, apart perhaps from the convenience of being able to visually monitor the state of the suppressor. However, it did provide the opportunity for other IC instrument vendors to offer chemically suppressed conductivity detection. This was significant from a *commercial* point of view, as the use of chemical suppression can result in lower detection limits than

are achievable with non-suppressed conductivity detection, particularly for anion analyses [27]. It also provided impetus for continued development in the area of packed-column mini-suppressors.

A more practical variation of the solid-phase chemical suppression approach, based on the same valve configuration shown in Fig. 8, was subsequently developed and was termed Electrochemically Regenerated Ion Suppression (ERIS). Here, the disposable cartridges were replaced with two solid-phase electrochemical suppressor cells [28,29] consisting of cation-exchange resin (in the case of anion analysis) or anion-exchange (resin in the case of cation-analysis) sandwiched between two porous platinum electrodes, which are connected to a constant current power supply. The eluent from the column passes through one cell, which functions as a normal packed-bed suppressor by virtue of the ion-exchange packing. The outlet from this cell is directed into the second cell, where regeneration of the ion-exchange resin occurs as a result of electrolysis of the water in the eluent. The electric field is applied only long enough to regenerate the small volume of packing material (14×7.5 mm I.D.) in the cell. The current is then turned off and the detector effluent continues to flow through the cell, purging it of any remaining gas bubbles and electrolysis products. The 10-port valve automatically switches at the end of every chromatographic run, which allows the freshly regenerated cell to suppress the eluent, while the spent cell is then regenerated electrolytically. Fig. 9 illustrates the suppression and electrochemical regeneration process occurring in each of the cells.

For anion analysis, the anode is connected to the inlet side of the cell to be regenerated. The detector effluent, typically water or carbonic acid, undergoes electrolysis when current passes through the cell. Oxygen gas and hydronium ions are generated at the anode and are carried into the cell, as shown above, converting the exhausted portion of the resin back into the hydrogen form. At the cathode, hydrogen gas and hydroxide ions are generated and carried to waste. Despite using different cells to suppress every alternative chromatographic run, retention time reproducibility of less than 0.5% RSD and peak area reproducibility of less than 6% RSD have been obtained for a total of 40 injections of a seven anion standard at low mg l^{-1} concentrations. In addition, the chromatographic efficiency obtained using the ERIS suppressor device was equivalent to that obtained using the self regenerating suppressor. The ERIS device also offers an advantage over the self regenerating, membrane-based suppressors in terms of its ability to tolerate higher back-pressures (up to 5000 p.s.i.).

A number of devices employing variations on the theme of the intermittently regenerated mini-column suppressor have become available commercially. These include the use of three small, packed-bed cartridges mounted in a rotor where the first cartridge is used as a suppressor for one chromatographic run, the second is regenerated with sulfuric acid, while the third is rinsed with water in preparation for the next run [30,31]. Yet another variation uses a single, small suppressor cartridge which is regenerated with sulfuric acid then rinsed with water prior to every run [24]. In this case the capacity of the suppressor is sufficiently low that displacing 1.0 ml of 0.25 *M* sulfuric acid from a loop through the cartridge is sufficient to regenerate the device prior to the next

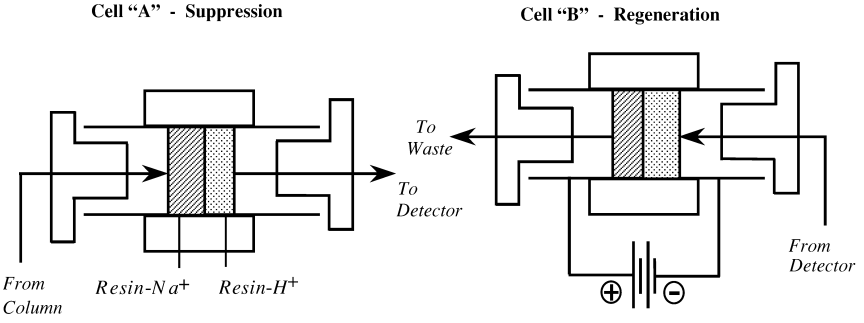

Fig. 9. Suppression and regeneration reactions for Electrochemically Regenerated Ion Suppression (ERIS). Adapted from Ref. [28].

chromatographic run. In both the devices described above, the sulfuric acid and water used to regenerate and rinse the suppressor cartridges is supplied with a peristaltic pump.

The major drawback of the intermittently regenerated mini-column suppressors described above is their lack of total suppression capacity. This means that they are not compatible with higher capacity separator columns and cannot be used for gradient separations which employ a significant change in the concentration of the eluting ion. The self regenerating, membrane-based devices described earlier are more commonly used in suppressed IC, by virtue of the fact that their higher suppression capacity permits use with a wider range of applications. A recent development, however, devised by Sato et al. [32], utilizes fresh cation-exchange resin with each run, deployed again using a rotor system, giving a switching valve suppressor. Since the suppressor valve is switched with each injection, regeneration is not required, with the ''used'' resin draining to waste whilst fresh resin is filled into the other port via pressure, ready for the next injection. This system has been found to provide minimal band broadening and increased chromatographic efficiency compared with a micromembrane suppressor. Additionally good reproducibility was obtained although the system was tested using isocratic eluents only.

5.3. Continuously regenerated packed-column suppressors

A further variation of the packed-column suppressor which provides the benefits of continuous regeneration and the ability to withstand high back pressures has been described by Small and Riviello [33]. This suppression device is based on the principles of ''ion reflux'', which is an ion-exchange technique where water is passed through an electrically polarized resin bed and electrolysis reactions are used to generate the eluent and also provide the means of suppression. An ion-reflux suppressor device comprises a small bed of high capacity, cation-exchange resin confined between two electrodes in a rigid polymer body, as shown in Fig. 10. The cathode and anode are placed in chambers that are separated from the main resin bed by cation-exchange membranes which permit electromigration

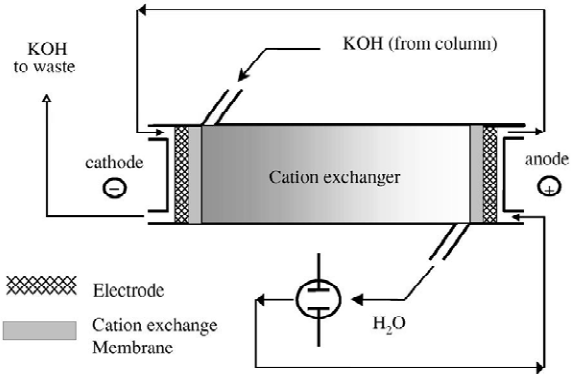

Fig. 10. Ion reflux-based, continuously regenerated suppressor. Adapted from Ref. [55].

of cations but prevent fluid flow between the electrode compartments and the resin bed. The electrode compartments allow entry and exit of the cell effluent in order to sweep out the products of electrolysis. The eluent (in this case KOH) is introduced (and exits) the main body of the device in such a way as to allow maximum contact with the membrane surface.

Polarization of the resin bed generates hydronium ions at the anode, which migrate in the opposite direction to the flow of eluent and displaces the incoming potassium ions toward the cathode chamber membrane. The potassium ions pass through the membrane into the cathode compartment, where they acquire an equivalent amount of hydroxide ions from the electrolysis reaction occurring in this compartment. As long as sufficient hydronium ions are generated at the anode to completely displace the incoming potassium ions across into the cathode chamber, the exit end of the device is always in the hydronium form, hence the eluent leaving the device will be suppressed. This device, which has recently become available commercially, combines the benefits of electrolytic self-regenerating suppressors and packed-column mini-suppressors in that it is continuously regenerated, has reasonably high dynamic suppression capacity and can tolerate high back-pressures. A further advantage of this device is lower baseline noise compared to the electrolytic SRS operated in the recycle mode (approximately 1 $nS\,cm^{-1}$ per min of measured response compared to about 4 $nS\,cm^{-1}$ per min of

measured response for the SRS with a typical carbonate–bicarbonate eluent).

An alternative approach to continuously electrochemically regenerating a packed bed suppressor has been suggested recently by Saari-Nordhaus and Anderson [34] for anion-exchange chromatography (Fig. 11). In this instance, the eluent and analyte ions undergo an acid–base neutralization reaction in the suppressor cell (as occurs in all IC suppressors) and a current applied continuously across the suppressor cell anode generates H^+ and oxygen gas, and at the cathode OH^- and hydrogen gas are generated, from water present in the cell. Subsequently, the H^+ ions generated at the anode flow across the cation-exchange packing, forcing sodium ions (the eluent used is in sodium form) from the eluent and cations from the sample to move toward the cathode. Hydroxide and/or carbonate salts, hydrogen gas and a portion of the analyte ions in the H^+ form exit through the anode. Water (if a hydroxide eluent) or carbonic acid (if a carbonate–bicarbonate eluent) and a portion of the analyte ions exit through the detector outlet. However, before reaching the detector, this cell effluent enters a degassing chamber, which is the novel feature of this suppressor. Carbonic acid, which is a significant problem when using carbonate eluents because it creates a baseline dip which interferes with early eluted analytes including fluoride, is removed in this degassing chamber. As the effluent flows through a degassing membrane, the carbonic acid dissociates to form carbon dioxide and water, the CO_2 diffusing through the membrane. This effectively removes all the carbonic acid from the suppressor effluent, additionally reducing the background conductivity from about 20 μS to around 1–2 μS, which improves detection sensitivity and baseline stability. Strong carbonate–bicarbonate eluents can therefore be used.

It should be noted that recently devised ion trap columns (Dionex), incorporated into the ion chromatographic system to remove trace ionic impurities from the eluent prior to reaching the analytical and guard columns, essentially act as polarized bed suppressors. As an example, anion trap columns in the hydroxide or borate form (ATC-3, ATC-HC) remove anionic contaminants by displacement with hydroxide or borate ions, resulting in a chemically suppressed eluent reaching the columns. These anion

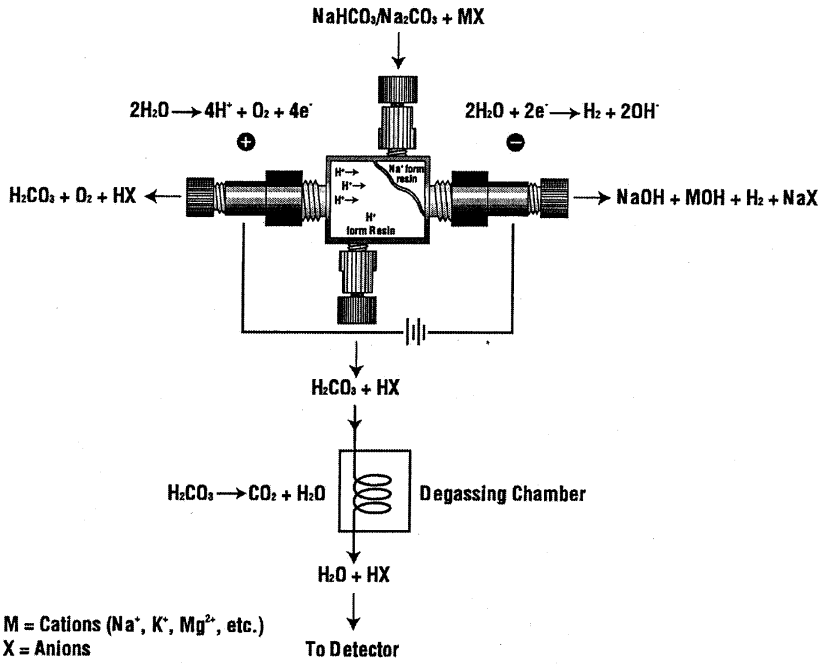

Fig. 11. Schematic diagram of the DS-plus suppressor Reproduced with permission from Ref. [34].

traps are then periodically regenerated off-line with fresh hydroxide or borate solutions.

5.4. Solid phase reagent suppression

A novel variation on the use of the packed-column suppressor is to eliminate the packed-column and add a colloidal suspension of ion-exchange resin directly to the eluent stream after the column in order to achieve the suppression reaction [35]. This approach, which was commercialized as ''solid-phase reagent (SPR)'' detection in the early-1990s, involves the addition of very small particles of high-capacity, cation-exchange resin (in the hydronium form) to the eluent stream using a conventional pneumatic post-column delivery module [36]. The particle size of the insoluble resin is small enough to keep it in suspension, yet the reagent itself is minimally conductive because of the low mobility of these particles and therefore makes only a small contribution to the background signal. Addition of such a suspension to an eluent of 2.8 m*M* sodium carbonate–2.2 m*M* sodium bicarbonate can reduce the background conductance from 624 to 18 $\mu S\,cm^{-1}$. Cations in the eluting band of analyte ions are replaced by hydronium ions in the same manner that occurs in conventional column suppressors and the peak response is therefore very similar to that observed using a conventional suppressor. This detection approach was shown to be suitable for the isocratic [35] and gradient [37] determination of common anions, the gradient separation of oxyhalides and well retained anions such as thiosulfate, citrate, and perchlorate [36], and for alkyl- and aromatic sulfonates using ionic strength/solvent gradients [37,38].

The major drawbacks of this approach are the expense of continuously supplying a 1% (w/v) suspension of the SPR at flow-rates of 0.4–0.7 $ml\,min^{-1}$, and the relatively high baseline noise obtained compared to a conventional anion micromembrane suppressor. Hence, this variation of chemical suppression has not been used widely in IC.

6. Post-suppressors

Post-suppressors are devices inserted between the suppressor and the detector for the purpose of further lowering the background conductance of the suppressed eluent or enhancing the detectability of the solute after the suppression reaction. When a carbonate buffer is used as eluent, the fully suppressed eluent contains H_2CO_3, which is dissociated partially in aqueous solution (to form H^+ and HCO_3^-) and so contributes to the background conductance. Moreover, the HCO_3^- present in the suppressed eluent also causes a reduction in the conductance of a sample peak by reaction with the H^+ ions which accompany the elution of the anion of a strong acid. It is therefore desirable if H_2CO_3 can be removed from the suppressed eluent.

This can be achieved by passing the suppressed eluent through a length of tubing which is permeable to carbon dioxide and can remove 90% of dissolved CO_2 [39]. In practice, the advantages which can be attained through the use of post-suppressors to remove H_2CO_3, which include decreased baseline conductance and noise, virtual elimination of the water dip, enhanced detectability of eluted anions, and the possibility of gradient elution can be achieved more easily through the use of hydroxide eluents and a suppressor device with sufficient dynamic capacity [40]. The widespread availability of hydroxide-selective anion-exchange columns, has mostly eliminated the use of post-suppressor devices to remove residual eluent carbonic acid in modern IC.

Post-suppressors can also be used to enhance the signal attributable to an analyte. Weak acid solutes (such as carboxylic acids) eluted from an ion-exclusion column by an acidic eluent are difficult to detect using direct conductivity measurements because they are eluted as their neutral or weakly ionized forms, which show little conductance. It therefore is beneficial to modify the eluted solutes if conductivity detection is to be employed. This can be accomplished by passing the suppressed eluent through a further suppressor, which replaces H^+ with a suitable cation and thereby enhances the ionization of the analyte. Cation-exchange membrane post-suppressors have been applied successfully for this purpose [41–44]. A suitable regenerant solution (such as tetrabutylammmonium hydroxide or dilute NaOH) leads to a reduction in the conductance of the acidic eluent and at the same time, ionization of the solute acids occurs. An interesting effect occurs if the

concentration of the NaOH regenerant is increased (e.g. from 10 to 500 m*M*). Under these conditions, the peak direction changes from positive (increasing conductance) for the 10 m*M* regenerant to negative (decreasing conductance) for the 500 m*M* regenerant [44]. The reason for this is that the more concentrated regenerant overcomes the Donnan exclusion effect of the cation-exchange membrane, so OH^- ions move into the eluent, giving a high background conductance. The eluted carboxylic acids react quantitatively with OH^-, causing a decrease in eluent conductance and hence indirect conductivity detection. This detection mode is more sensitive than direct conductivity because of the high limiting equivalent ionic conductance of OH^-.

The use of ion replacement post-suppressors has also been applied to enhance the detection of weak acids after separation by anion-exchange chromatography. Dasgupta and co-workers [45–48] installed a membrane converter after the conductivity detector to convert the (suppressed) weak acids to salts, which were then detected using a second conductivity detector. While this approach decreased the sensitivity for strong acid solutes by a factor of ~2, it enhanced the signal for weak acids by more than one order of magnitude. It was subsequently shown that reintroducing sodium hydroxide after the first detector converted the weak acids back to more conducting salts, which provided $\mu g\,l^{-1}$ level detection for solutes across the whole pK_a range [49].

Caliamanis and co-workers [50–52] used two micromembrane suppressors in series, the first operating as a conventional suppressor and the second operating as an ion replacement reactor, to enhance the detectability of weak acid anions, such as cyanide and borate. A schematic diagram of the instrumental arrangement (in this case for the detection of borate), and the fate of the weak and strong acid anions as they pass through the system, is shown in Fig. 12. Disodium EDTA was preferred over sodium hydroxide as the ion replacement reagent due to lower leakage of the forbidden anion across the cation-exchange membrane. The use of this approach with10 m*M* EDTA at pH 11 as the ion replacement reagent provided 850- and 3400-fold increases in peak height and area, respectively, for a 5.0 m*M* borate standard compared to using conventional suppressed conductivity detection.

It is interesting to note that operating the suppressor such that a sodium hydroxide eluent is not completely suppressed can result in sensitive detection for very weakly acidic analytes [53]. Use of a regenerant of low concentration (about one tenth of that of the eluent) results in the eluent being substantially, but not completely suppressed. The residual hydroxide in the eluent serves to fully ionise weakly acidic analytes, which appear as negative peaks. An alternative and unusual approach is to use indirect suppressed conductivity detection, where the eluent is converted into highly conducting species (i.e. the opposite of conventional suppressed conductivity detection) [54].

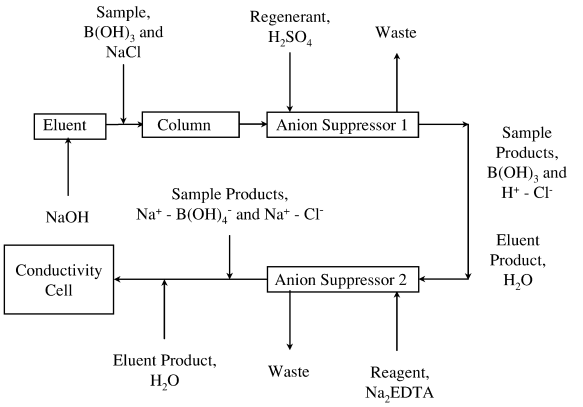

Fig. 12. Schematic diagram of the instrumental arrangement for post-suppressor enhancement of weak acids. Adapted from Ref. [51].

7. Conclusions

Currently there is a wide array of suppression devices available for the IC determination of inorganic ions, although the continuously regenerated high capacity micromembrane or packed column suppressors have become the most successful on a commercial basis. A significant advantage of these is that they are now practically maintenance free, whether regenerated electrolytically or by chemical means. This, together with developments in instrumentation over the years has meant that suppressed IC today is capable of both highly sensitive and stable conductivity detection, with the capability of unattended analysis for routine work, which is important from a cost effective perspective for many industrial and pharmaceutical companies.

Nevertheless, continual improvements to existing suppressor technologies are being driven by concurrent progress with novel stationary phases and subsequent eluent methodologies. It is envisaged that further improvements in suppressor design will continue, enabling the ongoing maturation of IC as the method of choice for inorganic ions.

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