Mechanisms: Ion Chromatography

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Introduction

The term ion chromatography (IC) does not refer to a single, specific chromatographic technique, but rather to the specialized application of a collection of established techniques. When introduced in 1975 IC referred only to the separation of inorganic anions and cations using a specific combination of ion exchange columns coupled to a conductimetric detector. Since that time, the definition of IC has expanded greatly and it can be best categorized in terms of the type of analytes separated rather than the manner in which the separation is achieved. We can therefore define IC to be:

> the use of liquid chromatographic methods for the separation of inorganic anions and cations and low molecular weight water-soluble organic acids and bases.

While a range of chromatographic methods (e.g. reversed-phase ion interaction chromatography) can be used to separate these types of analytes, it is true to say that the majority of IC separations are performed by ion exchange using specialized stationary phases. In the interests of brevity, the discussion of IC will therefore be confined to ion exchange methods only. The interested reader seeking a broader coverage of the technique is referred to any of the standard texts listed in the Further Reading section.

IC methods employing ion exchange can be divided somewhat arbitrarily into two main groups, largely on the basis of historical development and commercial marketing influences. These groups of methods are referred to as 'nonsuppressed ion chromatography' and 'suppressed ion chromatography'.

Nonsuppressed IC comprises all those methods in which an ion exchange column is used to separate a mixture of ions, with the separated analytes being passed *directly to the detector*. The hardware configuration employed is shown schematically in **Figure 1A**, from which it can be seen that this configuration parallels the hardware used in traditional high performance liquid chromatography (HPLC). Some of the alternative names proposed for this technique are:

1. single-column ion chromatography
2. electronically suppressed ion chromatography.

The first of these names indicates that only a single chromatographic column is employed and that the eluent is not *chemically* modified prior to entering the detector, whereas the second name pertains to the fact that the background conductance of the eluent can be cancelled *electronically* by certain types of conductivity detectors. 'Nonsuppressed IC' is the most frequently used term and is recommended.

The second group of ion exchange methods consists of those in which an additional device, called the *suppressor*, is inserted between the ion exchange separator column and the detector, as shown in **Figure 1B**. The function of the suppressor is to modify both the eluent and the analyte in order to improve the detectability of the analytes with a conductivity detector. The suppressor often requires a regenerant solution to enable it to operate for extended periods. Methods using this hardware configuration are referred to as:

1. suppressed ion chromatography
2. chemically suppressed ion chromatography
3. eluent-suppressed ion chromatography
4. dual-column ion chromatography.

The last of these names is misleading because modern suppressors are not columns, but rather flow-through membrane devices. The term 'suppressed IC' is recommended.

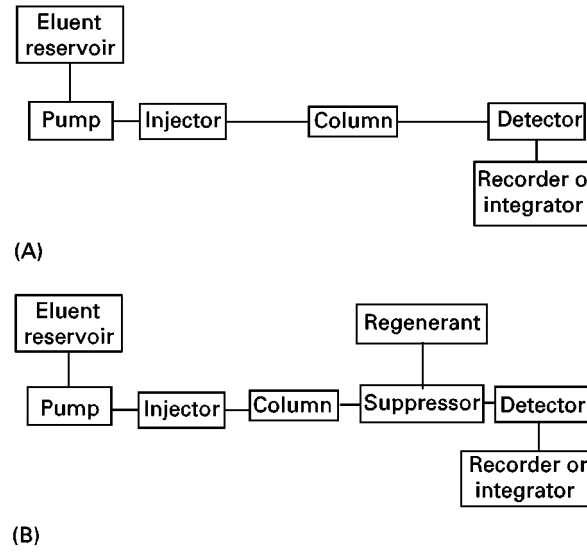

Figure 1 Block diagram showing the instrumental components used in (A) nonsuppressed and (B) suppressed IC.

Stationary Phases for IC

The ion exchange stationary phases used for IC are usually formed by chemical bonding of appropriate functional groups to a suitable substrate such as a polymer or silica. The functional groups used most commonly are sulfonates (for cation exchangers) and quaternary ammonium groups (for anion exchangers). In this respect, IC stationary phases are similar to the conventional ion exchange materials used widely throughout analytical chemistry. However, there are two important factors that differentiate the ion exchangers used in IC. The first is their ion exchange capacity. IC requires ion exchangers with low ion-exchange capacity, typically in the range 10–100 μequiv g^{-1}. This requirement can be attributed chiefly to the fact that IC was developed originally for use with conductivity detection, which introduces a preference for eluents of low background conductance in order to enhance the detectability of eluted analyte ions. The diversity of detection methods now available makes it possible to use columns of much higher ion exchange capacity, but because conductivity is still the most commonly employed detection mode, the majority of separations continue to be performed on low capacity materials. The second characteristic of ion exchangers for IC is their greatly enhanced chromatographic efficiency when compared to traditional ion exchangers.

In practice, both of the above-mentioned differentiating characteristics can be achieved by using ion exchangers in which the functional groups are confined to a thin shell around the surface of the stationary phase particle. This both reduces the number of functional groups (and hence the ion exchange capacity) and also limits the diffusion path of analyte ions, thereby improving mass-transfer characteristics and hence chromatographic efficiency. Two main approaches to synthesizing such ion exchangers can be identified. The first involves the use of only a very short reaction time during which the substrate material, i.e. either silica or a polymer such as poly(styrene-divinylbenzene) or poly(methyl methacrylate) is derivatized in order to introduce the ion exchange functional group. For example, a macroporous poly(styrene-divinylbenzene) bead immersed in concentrated sulfuric acid for less than 30 s will give a material in which sulfonic acid functional groups are confined to a very shallow depth (of the order of 20 nm) around the outside of the particle. This produces a 'surface-functionalized cation exchanger', represented schematically in **Figure 2**, in which the confinement of functional groups to the outer layer has been achieved by chemical means. Surface-functionalized anion exchangers can be produced in a similar manner. Historically, surface-functionalized ion exchangers have found most use in nonsuppressed IC.

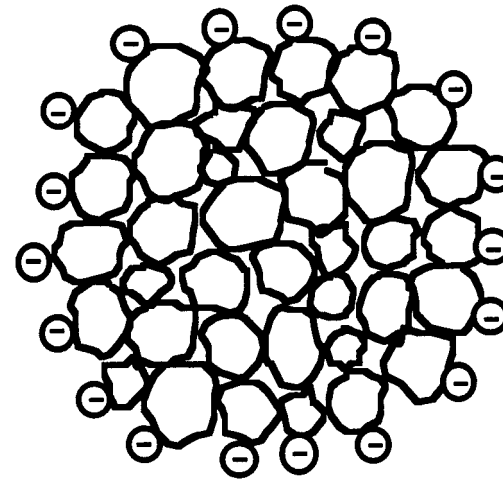

Figure 2 Schematic representation of the cross-section of a surface-sulfonated cation exchange resin. The negative charges represent sulfonic acid groups that are located on the surface of the resin bead. Note that the interior of the bead is not sulfonated.

The second approach to synthesis of ion exchangers for IC involves a physical process for confining the functional groups to the outer layer. These ion exchangers, known as 'agglomerated materials', consist of a central core particle, to which is attached a monolayer of small-diameter particles which carry the functional groups of the ion exchanger. Provided the outer layer of functionalized particles is very thin, the agglomerated particle exhibits excellent chromatographic performance due to the very short diffusion paths available to analyte ions during the ion exchange process. Schematic illustrations of agglomerated anion and cation exchangers are given in **Figure 3**. The central core (or support) particle is

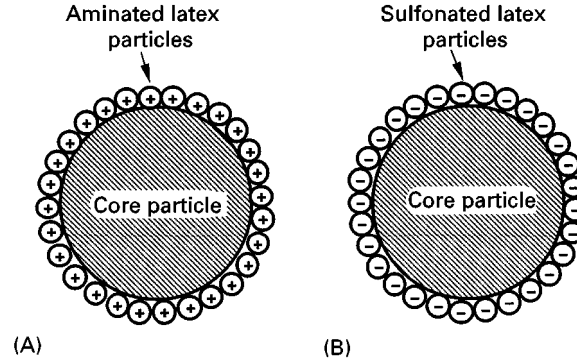

Figure 3 Schematic represenatation of agglomerated (A) anion and (B) cation exchangers.

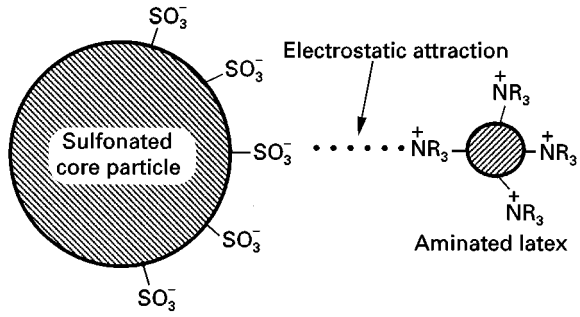

Figure 4 Formation of an agglomerated anion exchange resin using electrostatic binding. Note that the core and the latex particles are not drawn to scale.

generally poly(styrene-divinylbenzene) of moderate cross-linking, with a particle size in the range 7–30 μm, which has been functionalized to carry a charge opposite to that of the outer particles. The outer microparticles consist of finely ground resin or monodisperse latex (with diameters in the approximate range 20–100 nm) that has been functionalized to contain the desired ion exchange functional group. It is this functional group which determines the ion exchange properties of the composite particle, so that aminated (positively charged) latexes produce agglomerated anion exchangers (as illustrated in Figure 3A), while sulfonated (negatively charged) latexes produce agglomerated cation exchangers (Figure 3B). Electrostatic attraction between the oppositely charged core particles and outer microparticles holds the agglomerate together, even over long periods. **Figure 4** shows details of this electrostatic attraction for an agglomerated anion exchanger. Agglomerated ion exchangers are used most frequently in suppressed IC.

Mobile Phases for IC

Mobile phases (or eluents) for IC are similar to those used for regular ion exchange separations in that the eluent must contain a competing ion (of the same charge sign as the analytes to be separated) which serves to displace the analyte ions from the stationary phase and ultimately to elute the analytes from the column. However, eluents in IC must also satisfy the stringent requirement that they should be compatible with conductivity detection. In the case of nonsuppressed IC (in which the eluent is not involved in further reaction before reaching the detector) this means that eluent-competing ions of low limiting equivalent ionic conductance (see discussion of conductivity detection below) are required if direct conductivity detection is to be used. Aromatic carboxylates (such as benzoate and phthalate), aromatic sulfonates (such as toluenesulfonate) and complex ions (such as the anionic complex formed between gluconate and borate) are ideal for anion separations, whereas aromatic bases are useful for cation separations. All of these species are bulky ions having low ionic mobility (and hence low conductance) so that direct detection of more mobile analyte ions (such as chloride, sulfate, etc.) is possible using conductivity. Alternatively, indirect conductivity detection is possible using eluent-competing ions having very high values of limiting ionic conductance, such as hydronium ions for cation separations and hydroxide ions for anion separations.

Suppressed IC offers the opportunity for further reaction of the eluent before detection. The purpose of this reaction is to reduce the conductance of the eluent; in most cases acid–base reactions are used. The mechanism of eluent suppression will be discussed further below, but for the present it can be assumed that the process works best when applied to eluents comprising competing ions that can be easily neutralized in an acid–base reaction. For example, carbonate and bicarbonate (or mixtures of the two) can be used for anion separations, while dilute solutions of mineral acids can be used for cation separations.

Many cation separations cannot be achieved simply through correct choice of a suitable eluent-competing cation. Polyvalent cations show such strong electrostatic attraction to sulfonic acid cation exchangers that they can only be displaced by using concentrated eluents. This, in turn, renders conductivity detection difficult. Practical alternatives are created by the use of a complexing agent as the eluent, or by the addition of a complexing agent to an eluent that already contains a competing cation. This serves the dual purpose of reducing the effective charge on the analyte cation (and hence its affinity for the cation exchange sites) and also introduces a further dimension of selectivity between analytes that does not exist when ion exchange is the only retention mechanism in operation. The above approaches are illustrated schematically in **Figure 5**, which shows the equilibria existing between a divalent metal analyte ion M^{2+}, a complexing agent (H_2L), and an ethylenediamine (en) eluent, at the surface of a cation exchange resin. In Figure 5A, the eluent contains only the ligand species. Retention of the analyte ion on a cation exchange resin is moderated by the complexation effect of the deprotonated ligand, which can be said to exert a *pulling* effect on the analyte. The eluent pH determines the degree to which the ligand is deprotonated, which in turn governs the retention of the analyte. Retention is also regulated by the type and concentration of the ligand. Tartrate, oxalate, citrate

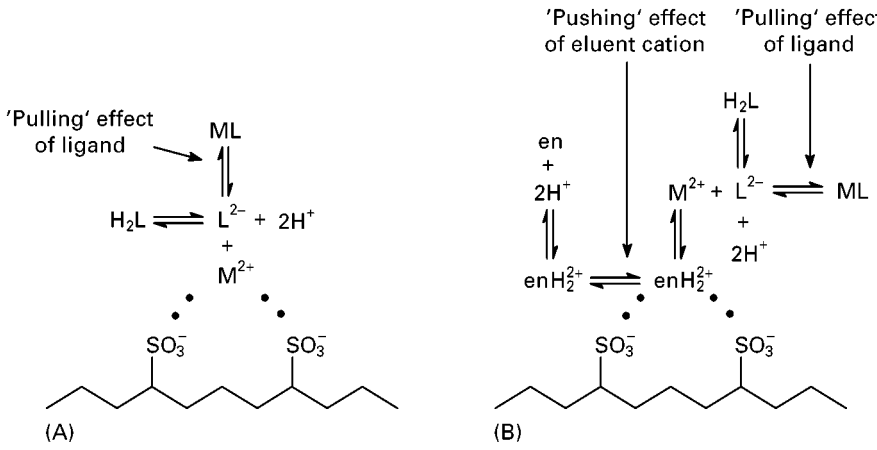

Figure 5 Schematic illustration of the equilibria existing between an analyte cation (M^{2+}), ethylenediamine (en) and an added ligand (H_2L) at the surface of a cation exchanger. In (A) the eluent contains only the ligand, while in (B) the eluent contains both ligand and ethylenediamine.

and α-hydroxyisobutyric acid are examples of typical ligands used as eluent additives.

Figure 5B shows the case where the eluent contains both a ligand and a competing cation (enH_2^{2+}). The retention of the analyte ion, M^{2+}, is influenced by the competitive effect for the sulfonic acid groups exerted by enH_2^{2+}, and also by the complexation of M^{2+} by the deprotonated ligand L^{2-}. Once again, complexation reduces the effective concentration of M^{2+} and the analyte is therefore less successful in competing for the cation exchange sites. This shows that elution of the analyte results from a combination of the *pushing*, or displacement, effect of the competing cation in the eluent and the complexation, or *pulling*, effect of the complexing agent. The eluent pH influences both the protonation of ethylenediamine and the deprotonation of the added ligand, which in turn controls the degree of complex formation and hence the retention of the analyte. The type and concentration of the added ligand again play a major role in determining analyte retention. For analyte ions of similar ion exchange selectivities, the retention order closely follows the reverse sequence of the conditional formation constants for the analyte–ligand complexes.

Detection in IC

As discussed earlier, the majority of IC separations are performed in conjunction with conductivity detection. However, two further modes of detection, namely indirect UV spectrophotometry and post-column reaction with visible spectrophotometry, also find widespread use. Each of these detection modes will be described briefly.

The normal mode of operation of a detector in IC is the monitoring of a signal (due to the analyte), which appears as an *increase* above the background signal arising from the eluent alone. This is called *direct detection*, and is a useful detection mode whenever the background detector signal due to the eluent alone is small enough to be offset by the zeroing control on the detector. An alternative, namely *indirect detection*, is also possible and involves the measurement of a *decrease* in detector signal when the analyte is eluted and is generally used with eluents that give a high background signal. To function correctly, indirect detection requires that the background composition of the mobile phase must alter in the presence of the eluted analyte and it is this change, rather than a specific characteristic of the analyte itself, that is monitored. Ion exchange chromatography is the most important example of a separation mode that is suited to indirect detection.

Conductivity Detection

Conductivity detection is an important example of bulk property detection and is used commonly when the eluted analytes are ionic, for example acids and bases. However, the major use of this form of detection is for inorganic anions and cations after their separation by ion exchange chromatography. Conductivity detection is universal in response for such analytes, and the detectors themselves are relatively simple to construct and operate.

A solution of an electrolyte will conduct an electrical current if two electrodes are inserted into the solution and a potential is applied across the electrodes. It is relatively straightforward to show that the conductance of a solution, G (having the units of

microsiemens, represented by the symbol μS) is given by:

$$G = \frac{1000\Lambda C}{K} = \frac{\Lambda C}{10^{-3}K} \quad [1]$$

where Λ is the limiting equivalent conductance of the electrolyte (with units S cm^2 equiv^{-1}), C is the concentration of the electrolyte, expressed as equivalents per litre of solution (equiv L^{-1}), and K is the cell constant (with units of cm^{-1}) determined by the geometry of the electrodes. The conductance can be seen to be proportional to the equivalent conductance of the electrolyte and its concentration. In addition, the lower the cell constant, the higher the conductance. This occurs for cells with large surface area electrodes which are close together.

Since the conductance of the solution results from both the anions and cations of the electrolyte, we must therefore calculate conductance using values for the limiting equivalent ionic conductances (λ) of the individual anions and cations in solution. Equation [1] can now be rewritten as:

$$G = \frac{(\lambda_+ + \lambda_-)C}{10^{-3}K} \quad [2]$$

where λ_+ and λ_- are the limiting equivalent ionic conductances of the cationic and anionic components of the electrolyte, respectively. Limiting equivalent ionic conductances for some common ionic species are listed in **Table 1**.

The operating principles of conductivity detection can be illustrated by considering the conductance of a typical eluent prior to and during the elution of an analyte ion. The conductance change, ΔG, produced when an anionic analyte S^- is eluted by an anionic eluent E^-, is given by:

$$\Delta G = \frac{(\lambda_{S-} - \lambda_{E-})C_S I_S}{10^{-3}K} \quad [3]$$

where C_S is the concentration of the analyte and I_S is the fraction of the analyte present in the ionic form. Equation [3] shows that the detector response depends on analyte concentration, the difference in the limiting equivalent ionic conductances of the eluent and analyte anions, and the degree of ionization of analyte. The last of these parameters is generally governed by the eluent pH.

Sensitive conductivity detection can result as long as there is a considerable difference in the limiting equivalent ionic conductances of the analyte and eluent ions. This difference can be positive or negative, depending on whether the eluent ion is strongly or weakly conducting. If the limiting equivalent ionic conductance of the eluent ion is low, then an increase in conductance occurs when the analyte enters the

Table 1 Limiting equivalent ionic conductances of some ions in aqueous solution at 25°C

Anion	λ_- *(S cm^2 equiv^{-1})*	*Cation*	λ_+ *(S cm^2 equiv^{-1})*
OH^-	198	H_3O^+	350
$Fe(CN)_6^{4-}$	111	Rb^+	78
$Fe(CN)_6^{3-}$	101	Cs^+	77
CrO_4^{2-}	85	K^+	74
CN^-	82	NH_4^+	73
SO_4^{2-}	80	Pb^{2+}	71
Br^-	78	Fe^{3+}	68
I^-	77	Ba^{2+}	64
Cl^-	76	Al^{3+}	61
$C_2O_4^{2-}$	74	Ca^{2+}	60
CO_3^{2-}	72	Sr^{2+}	59
NO_3^-	71	$CH_3NH_3^+$	58
PO_4^{3-}	69	Cu^{2+}	55
ClO_4^-	67	Cd^{2+}	54
SCN^-	66	Fe^{2+}	54
ClO_3^-	65	Mg^{2+}	53
$Citrate^{3-}$	56	Co^{2+}	53
$HCOO^-$	55	Zn^{2+}	53
F^-	54	Na^+	50
HCO_3^-	45	$Phenylethylammonium^+$	40
CH_3COO^-	41	Li^+	39
$Phthalate^{2-}$	38	$N(C_2H_5)_4^+$	33
$C_2H_5COO^-$	36	$Benzylammonium^+$	32
$Benzoate^-$	32	$Methylpyridinium^+$	30

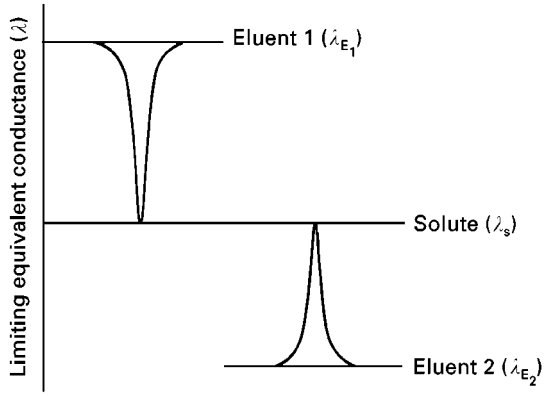

Figure 6 Schematic illustration of the principles of direct and indirect conductivity detection.

detection cell. This detection mode is *direct*, since the analyte has a *higher* value of the measured property than does the eluent ion. Alternatively, an eluent ion with a high limiting equivalent ionic conductance can be employed and a decrease in conductance would occur when the analyte enters the detection cell. This type of detection is *indirect*, where the analyte has a *lower* value of the measured property than does the eluent ion. These detection modes are shown schematically in **Figure 6** and practical examples of direct and indirect conductivity detection are illustrated in **Figures 7** and 8. In Figure 7A, the weakly conducting borate–gluconate complex is used as eluent, whilst in Figure 7B a suppressed carbonate–bicarbonate eluent is used (see below). In contrast, highly conducting eluent ions are used in Figure 8, namely hydroxide (Figure 8A) and hydronium (Figure 8B) ions. Examination of Table 1 shows that these are the most strongly conducting ions and should therefore lead to sensitive indirect conductivity detection.

Use of Suppressors with Conductivity Detection

When the conductivity detector is mounted in the usual position for a chromatographic detector, that is immediately after the column, the choice of eluent composition must also take into account the requirements for sensitive conductimetric detection. In many cases, the requirements of conductivity detection also impose constraints on the characteristics of the column used. One way to diminish this interdependence between column, eluent and detector is to insert a device between the column and detector that can chemically or physically modify the eluent. A commonly used device of this type is a suppressor, which achieves signal enhancement in conductivity detection by reducing the conductance of the eluent and simultaneously increasing the conductance of the sample band.

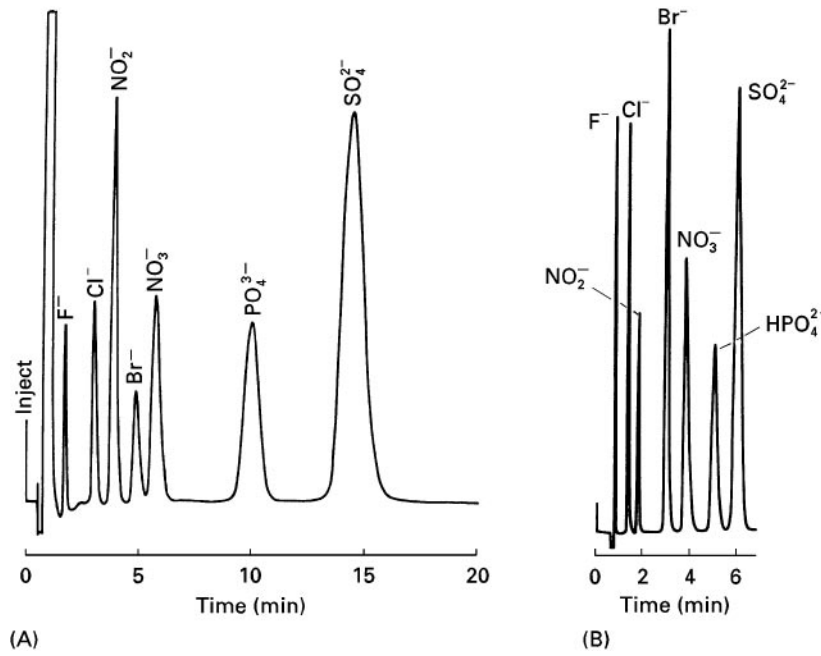

Figure 7 Direct conductivity detection employed in the separation of anions using (A) nonsuppressed and (B) suppressed ion chromatography. (A) A Waters IC Pak A surface-functionalized anion exchange column was used with gluconate–borate as eluent. (B) A Dionex HPIC-AS4A agglomerated anion exchange column was used with a carbonate–bicarbonate eluent. (Chromatograms courtesy of Waters and Dionex.)

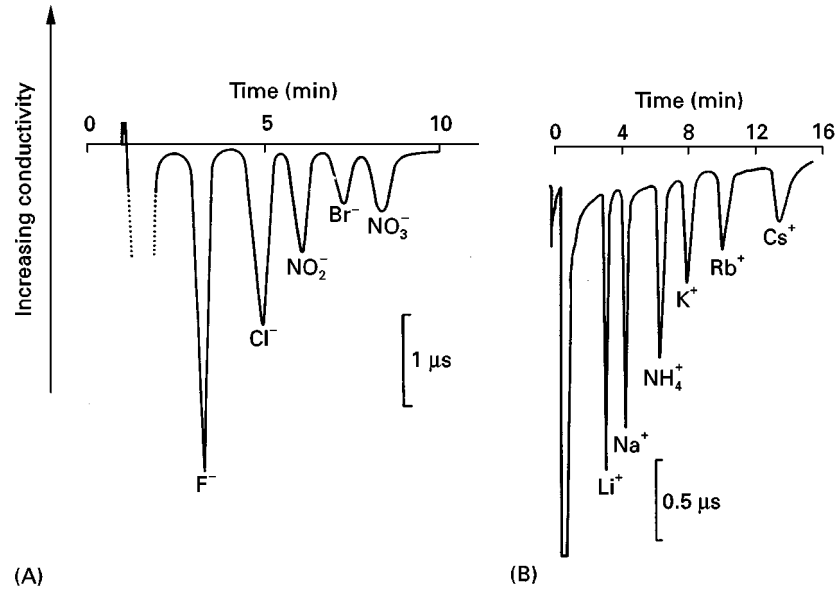

Figure 8 Indirect conductivity detection of (A) anions and (B) cations. (A) A TSK-GEL 620 SA surface-functionalized polymethylmethacrylate anion-exchange column was used with 2 mmol L^{-1} KOH as eluent. (Reprinted with permission from Okada and Kuwamoto, 1983.) (B) A Waters IC Pak C surface-functionalized poly(styrene-divinylbenzene) cation exchange column was used with 2 mmol L^{-1} HNO_3 as eluent. (Chromatogram courtesy of Waters.)

The operation of a suppressor can be illustrated by considering the elution of chloride ion with an eluent of $NaHCO_3$. If the suppressor is capable of exchanging sodium ions in the eluent with hydrogen ions from the suppressor, the first of the reactions below occurs (reaction [I]). The HCO_3^- ions are converted into weakly conducting H_2CO_3, and the background conductance of the eluent is said to be suppressed. At the same time, the eluted analyte (in this case, chloride) will also undergo the second of the reactions below in the suppressor (reaction [II]).

$$\text{Suppressor–H}^+ + \text{Na}^+\text{HCO}_3^- \rightleftharpoons \text{Suppressor–Na}^+ + \text{H}_2\text{CO}_3 \qquad [\text{I}]$$

$$\text{Suppressor–H}^+ + \text{Na}^+ + \text{Cl}^- \rightleftharpoons \text{Suppressor–Na}^+ + \text{H}^+ + \text{Cl}^- \qquad [\text{II}]$$

The combined result of these processes is that the eluent conductance is decreased greatly, while 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 analyte is therefore enhanced considerably.

It is important to note that suppression reactions are not limited to acid–base reactions, such as those shown in the above examples, nor are they limited to the detection of anions. Indeed, any post-column reaction that results in a reduction of the background conductance of the eluent can be classified as a suppression reaction. However, the ensuing discussion of suppressor design and performance will be restricted to those which employ acid–base reactions, since these are the most widely used.

Modern suppressors are based on dialysis reactions occurring through ion exchange membranes, with the membrane being generally used as a flat sheet. **Figure 9** gives a schematic representation of the design of a typical flat-sheet (or 'micromembrane') suppressor. The eluent contacts one side of the membrane while a regenerant solution flows in a countercurrent direction on the opposite side of the membrane. In the case of the bicarbonate eluent considered earlier, the membrane would be a cation exchanger and the regenerant would be a solution containing H^+ ions. The eluent passes through a central chamber that 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 that 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), so band-broadening is minimal.

The mode of operation of the suppressor with a $NaHCO_3/Na_2CO_3$ eluent is illustrated schematically in **Figure 10A**. Sodium ions from the eluent diffuse through the cation exchange membrane and

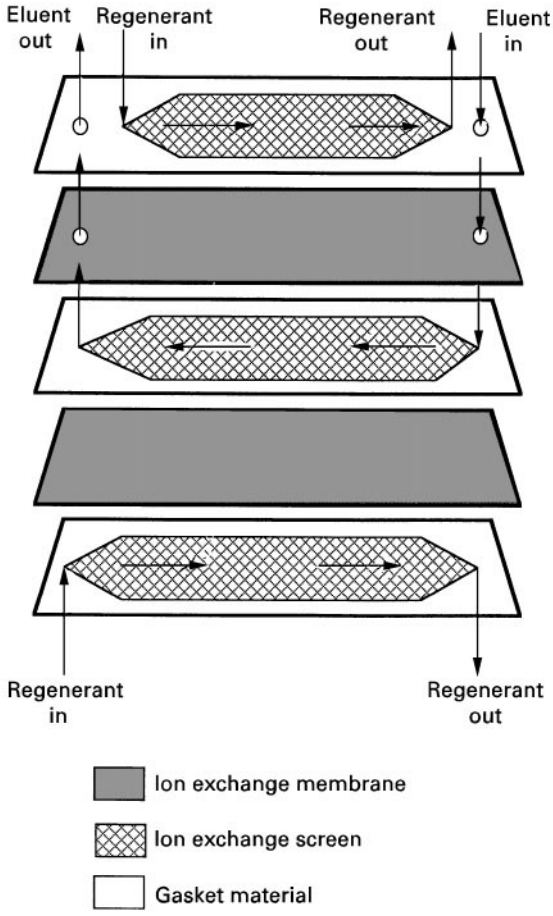

Figure 9 Design of a micromembrane suppressor.

are replaced by H^+ ions from the regenerant, producing the desired suppression reaction. Analyte anions (e.g. chloride) are prevented from penetrating the membrane by the repulsion effect of the anionic functional groups of the membrane and therefore remain in the eluent stream. A schematic representation of the operation of this type of suppressor in the separation of cations using a hydrochloric acid eluent and a barium hydroxide regenerant solution is shown in **Figure 10B**.

The micromembrane suppressor combines the advantages of other suppression devices, while at the same time eliminating their drawbacks. These advantages can be summarized as:

1. small internal volume, leading to minimal band-broadening effects and hence low detection limits;
2. continuous regeneration;
3. high dynamic suppression capacity, which can be varied readily by changing the nature, concentration and flow-rate of the regenerant;
4. suitable for gradient elution with appropriate eluents;
5. resistant to many organic solvents and ion interaction reagents; and
6. a wider choice of eluent types is possible because of the high dynamic suppression capacities that can be achieved.

A recent adaptation of the micromembrane suppressor replaces the flowing regenerant solution with

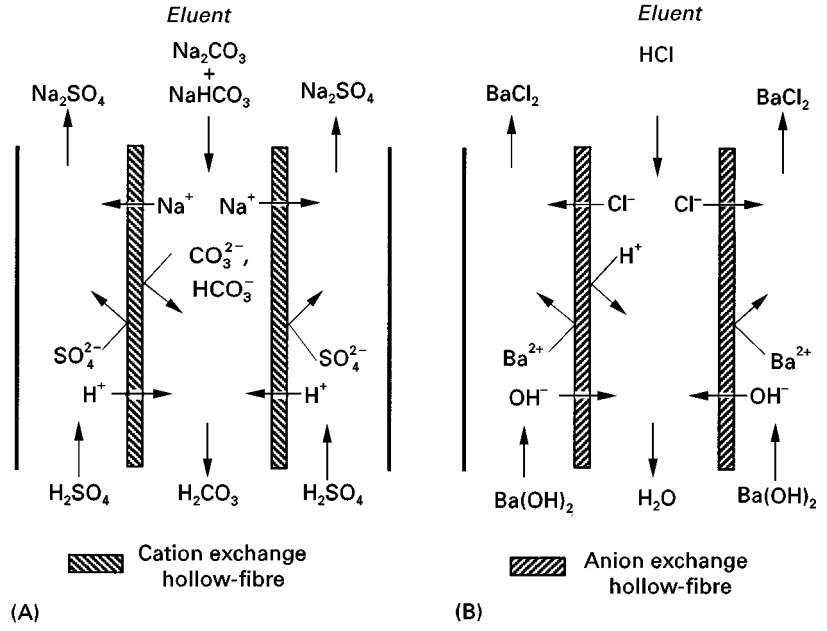

Figure 10 Schematic operation of a micromembrane suppressor for eluents used with (A) anion exchange and (B) cation exchange chromatography.

water and inserts electrodes into the two regenerant compartments. This water is then electrolysed in the regenerant compartments to produce the hydronium and hydroxide ions necessary for the suppression reactions. In addition, the electric field applied to achieve the electrolysis also provides enhanced movement of ions across the membranes and thus more efficient suppression is achieved.

Indirect Spectrophotometric Detection of Anions

Indirect spectrophotometric detection is applied most frequently to the detection of anions and will therefore be discussed in this context only. When an anionic analyte S^{x-} is eluted from an ion exchanger by an eluent containing a competing anion E^{y-}, the absorbance change ΔA is given by:

$$\Delta A = \left(\varepsilon_{S^{x-}} - \frac{x}{y} \varepsilon_{E^{y-}} \right) C_S m \qquad [4]$$

where $\varepsilon_{S^{x-}}$ and $\varepsilon_{E^{y-}}$ are the molar absorptivities at the detection wavelength of the analyte and eluent anions, respectively, C_S is the molar concentration of the analyte and m is the detector pathlength in cm. We see that the absorbance change measured by the detector on elution of an analyte is proportional to the analyte concentration, the cell pathlength and to the difference in molar absorptivities between the analyte and eluent anions. Equation [4] shows that indirect detection will result when the molar absorptivity of the analyte anion is less than that of the eluent anion, leading to a negative value for ΔA.

Indirect spectrophotometric detection, also called indirect photometric chromatography and vacancy detection, is a very widely used detection method in IC. Decreased absorbance accompanies the elution of analytes, but the polarity of the detector output is often reversed in order to give positive peaks on the recorder. Provided that Beer's law is followed, then linear calibration plots will result, thereby permitting sample quantification. Eluents such as phthalate, nitrate, sulfobenzoate and benzenetricarboxylate are commonly used for the separation of anions. A typical chromatogram obtained with phthalate as the eluent is shown in **Figure 11**.

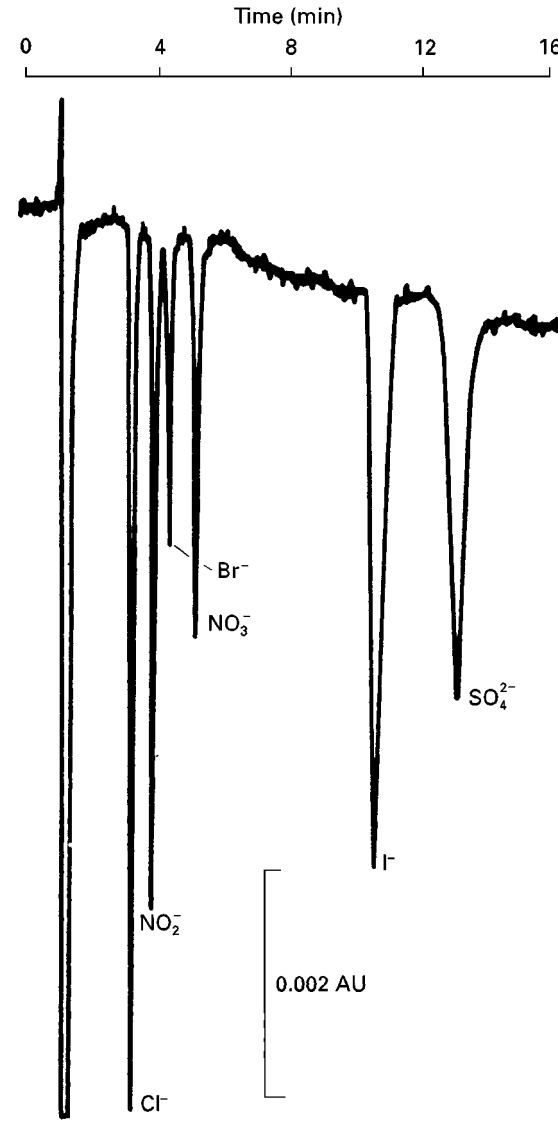

Figure 11 Detection of anions using indirect spectrophotometry. A Vydac 302 4.6 IC surface-functionalized silica anion exchange column was used with 5 mmol L^{-1} potassium hydrogen phthalate at pH 4.0 as eluent. Detection was at 285 nm. (Reprinted with permission from Heckenberg and Haddad, 1984.)

Post-column Reaction Detection of Cations

While alkali metal and alkaline earth cations are detected routinely using conductivity detection, transition metals and lanthanoids are most commonly detected using a post-column reaction (PCR). In most cases, this involves a post-column addition of a colour-forming ligand, generally a metallochromic dye. Typical examples of such dyes are 4-(2-pyridylazo)resorcinol (PAR), which is used for the detection of transition metals, and 2,7-bis(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (Arsenazo III), which is used for the detection of lanthanoids. Both dyes react rapidly with a wide range of metal ions to form strongly absorbing complexes that facilitate sensitive detection without the need for complicated reactors or mixing devices. **Figure 12** shows a typical chromatogram obtained using Arsenazo I as the PCR reagent.

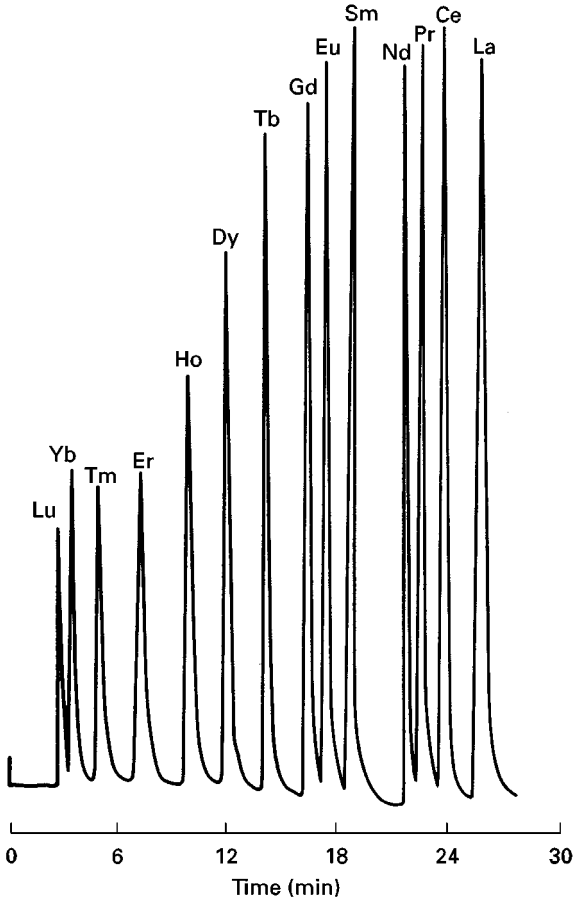

Figure 12 Use of post-column reaction for the detection of lanthanoids. Separation was achieved on a Nucleosil 10SA silica-based cation exchange column using 2-methyllactic acid as eluent, with post-column reaction detection with Arsenazo I. (Reprinted with permission from Wang *et al.*, 1984.)

Analytical Performance of IC

IC is now a relatively mature analytical technique and has found application across a wide range of analytes and sample types. Almost all inorganic anions can be determined using IC, as can the alkali metal cations, alkaline earth cations, the first row transition metals and the lanthanoids. However, the availability of sensitive, multielement spectroscopic analytical techniques for the measurement of cations has meant that the major focus of IC has been in the area of anion analysis. About 80% of publications on IC fall into this area.

Variation of the nature of the functional group on the stationary phase can be used as a means to manipulate separation selectivity in IC. For this reason there exists a wide range of stationary phases, and more than 150 different types of IC column are available commercially. It is therefore usually possible to identify a stationary phase suitable for most practical separations. Chromatographic efficiencies of these columns are typically of the order of 1500 theoretical plates for a 5 cm column packed with a surface functionalized material, and 4500 theoretical plates for a 25 cm column packed with an agglomerated material.

Detection limits are dependent on the particular analyte ion and on the detection mode used. However, if one considers only conductivity detection, then detection limits of 10 ppb (for a 50 μL injection) and 100 ppb (for a 100 μL injection) are achievable for suppressed and nonsuppressed IC, respectively. When lower detection limits are required, on-line sample enrichment using a small ion exchange preconcentrator column can be employed, leading to detection limits which are in the ppt range.

IC has found application to a very wide range of samples, but a survey of the literature reveals that the most common application areas are environmental analysis (especially of air and aerosol samples and various natural waters), industrial analysis (such as wastewaters and process samples from pulp and paper manufacture), food and plant analysis, and clinical and pharmaceutical analysis.

See also: **II/Ion Exchange. II/Chromatography: Liquid:** Detectors: Ultraviolet and Visible Detection. **Ion Analysis:** Liquid Chromatography. **Ion-Exclusion Chromatography: Liquid Chromatography. Metal Complexes:** Ion Chromatography.

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