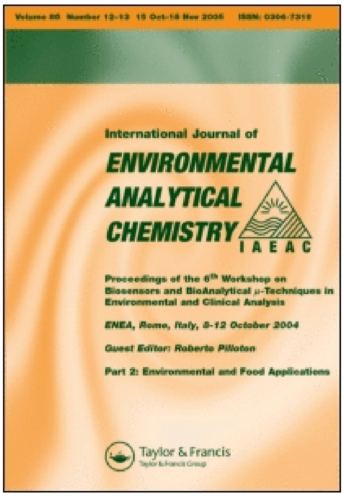

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Principles of Detection in Single-Column Ion Chromatography[†]

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At one time or another virtually every type of detector has been used for ion chromatography. But, in order for these detectors to operate, certain fundamental criteria of the separation column (and the separation mechanism), eluant, and sample must be met. If an ion-exchange process is used to separate the ions, then detection of the ions is based on the difference in detector response of the sample and eluant ions. This phenomenon, which is universal for all detectors, is based on the fact that the sample ion replaces the eluant ion during the elution process. In ion-exclusion chromatography, the elution of a sample species involves an addition of the sample to the eluant. Thus equations describing this behaviour are quite different to ion-exchange ion chromatography.

KEY WORDS: Single-column ion chromatography, detector, detection, ion chromatography, eluant, ion exchange, ion exclusion.

INTRODUCTION

The first paper describing single-column ion chromatography (SCIC) explained the principles of detection in a fairly simple, non-mathematical way. Unlike suppressor ion chromatography which employed a suppressor to lower the background signal, the eluants

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in single-column ion chromatography were chosen to already have a low background conductivity. This choice of a low conductivity eluant allowed the sensitive conductometric detection of common inorganic and organic sample anions.[1,2] As more papers were published on SCIC, it was shown that the primary factor for eluant selection was not that the eluant ions have a low background (or a low equivalent) conductance. The most important factor was that the eluant ions have a *different* equivalent conductance than the sample ions. In fact, the eluant could have a high background conductivity and still be used for SCIC. This was first shown for cation chromatography where a nitric acid eluant was used to separate alkali metals. As the sample ions eluted, the peaks were recorded as a decreasing conductivity chromatogram.[3] Later, a hydroxide eluant was used to demonstrate the same type of conductivity detection for weak acid anion separations. Hydroxide has a very high equivalent conductance compared to common anions and chromatograms with this eluant are also recorded as decreasing conductivity peaks.[4]

Many papers that have been written in the past few years on SCIC have included mathematical discussions on the principles of detection and detector response and sensitivity of ion chromatography. The first work was with conductivity detection. Now, however, many detectors including refractive index,[5,6] spectrophotometric,[7–9] electrochemical[10,11] and others have been used for single-column ion chromatography. Many of the papers describing these detection methods have discussed the principles of ion detection. The purpose of this paper is to describe the general principles of detection for single-column ion chromatography regardless of the detector employed. Limitations and advantages of the various detectors will be discussed. Most of this paper centers around the use of ion-exchange chromatography as the separation mechanism. Ion exchangers are the most useful and popular columns for ion chromatography. However, some discussions include ion-interaction (ion-pair) and ion-exclusion chromatography. Many of the detection principles described in this paper also apply to suppressor ion chromatography.

DEFINITIONS

In order to describe accurately the various detection principles and processes, it is necessary to define ion chromatography. Ion chromatography is simply the high performance liquid chromatographic (HPLC) separation and detection of ions.[4] The term implies that the separations are rapid and that the detection is performed continuously and automatically. No restriction is placed on either the type of separation mechanism or the type of detector that is employed for the ion determinations.

There are three major types of ion chromatography: single column, suppressor and post-column reactor. Single-column ion chromatography is performed with the separation column connected directly to the detector cell (Figure 1). Suppressor ion chromatography employs a suppressor between the column and a conductivity detector. The suppressor reduces the background conductivity

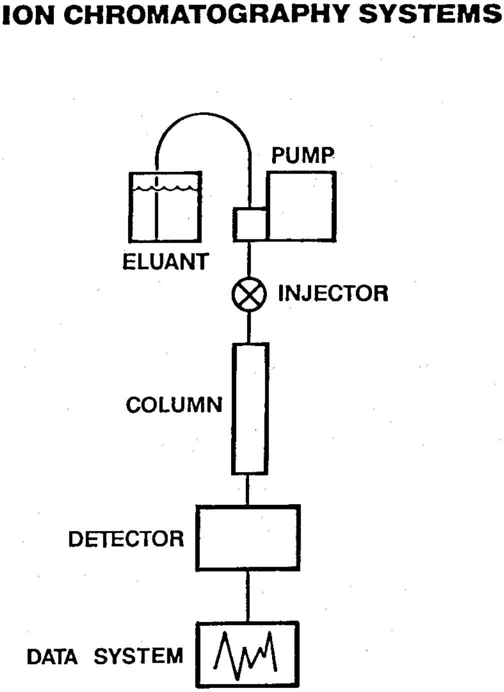

FIGURE 1 Schematic representation of a liquid chromatograph for single-column ion chromatography.

of the eluant. The sample ion peaks are detected by conductivity. Post-column reactor ion chromatography uses a color-forming reagent to react with sample ions to form detectable species. Details of the differences between these different types of ion chromatography have been described elsewhere.[4]

The term, detector response, refers to the change in signal that is directly related to the change in sample concentration. Detector response is technically identical to the term sensitivity. None of the discussions in this paper refer to signal-to-noise ratios (or detection limits). This is because it is difficult to predict the noise level in a particular ion chromatographic method or system.

GENERAL DETECTION PROCESS

There are two important parameters in an ion chromatographic system: the detector type and the column type. Virtually every type of detector imaginable has been used for SCIC. However, in order to derive a general equation for detector response we shall first use conductivity detection as an example. In general, the detector type does not affect the derivation of the equations. There are a few exceptions which will be discussed later.

Many different types of separation mechanisms have been used for SCIC. Ion exchange is the most popular, but ion interaction and ion exclusion chromatography have also been used extensively. Unlike the detector type, the separation mechanism does affect the general equation of detection in SCIC. Because ion exchange chromatography is the most useful for ion chromatography, the equations will first be derived with this column type.

The discussions regarding detector response in ion-exchange chromatography also apply, at least to a certain extent, to detector response in ion-interaction chromatography. The use of ion-pairing reagents has the appearance of converting a reverse phase column into an ion exchanger. The effect of changing ion-pairing reagent concentrations is related to the effect of changing resin capacity in ion-exchange chromatography.[12] However, the equilibria of changing the pH and concentration of the eluant and sample solutions are much more complicated in ion-interaction chromatography. "Sorption" of the ion-pairing reagent on the column can be affected by injection of the sample. However, equations developed for ion-exchange chromatography can apply to ion-interaction chromatography.

The ion-exchange process

Taking the example of anion chromatography, when a sample containing a series of solute sample anions and their counter cation(s) are injected, the anions are taken up by the anion exchanger. This causes an equivalent amount of eluant anions to be displaced and go into solution. The sample counter cation and the eluant anions "sample plug" resulting from the injection pass quickly through the column and elute as a psuedo or matrix peak. After the sample plug has passed, the baseline is quickly restored to that obtained with the eluant alone. However, the solute anions gradually move down the column, pushed by the mass-action effect of the eluant anion of the ion-exchange equilibrium. The total anion concentration in solution is fixed by the eluant anion concentration because a solute anion can enter the solution phase only by uptake of equivalent number of eluant anions. Thus ion chromatography performed by ion exchange is a *replacement process.* A sample peak is really composed of both sample and eluant ions. The ionic concentration (normality) of the peak is constant and equal to the eluant concentration, but (of course) the identity of the ions change as the peak is eluted.

Derivation of general equation

The replacement process and peak detection in ion exchange can be expressed mathematically. Using the equation for solution conductance, the background signal due to the eluant is expressed below.

Background signal:

$$G_1 = (\Lambda_E C_E) 1/K$$

where G is the solution conductance, Λ is the equivalent conductance of the eluant anion and cation ion pair, C_E is the concentration of the eluant and K is a cell constant that corrects for differences in detector cells.

The following equation can be used to describe the solution conductance of a sample peak.

Conductance of a sample peak:

$$G_2 = (\Lambda_E(C_E - C_S))1/K + (\Lambda_S C_S)1/K$$

where E denotes eluant and S denotes sample ions. The first term in the equation is due to the eluant contribution. The sample concentration is subtracted from the eluant concentration which reflects the replacement of sample ions for eluant ions on the ion exchanger. The second term in the equation is due to the sample ion contribution

Detectors operate in a differential mode. When a sample peak elutes, the peak is due to the absolute conductance of the peak, G_2, minus the background signal, G_1. This is shown in the equation below.

Peak conductance:

$$\Delta G = G_2 - G_1 = ((\Lambda_S - \Lambda_E)C_S)1/K.$$

The identity of the counter ion is the same for both the eluant ion and the sample ions. Thus, the equation for peak conductance can be simplified.

Neglecting the conductance of the counter ion, peak conductance:

$$\Delta G = G_2 - G_1 = ((\lambda_{S^-} - \lambda_{E^-})C_{S^-})1/K$$

where λ is the equivalent conductance of each particular ion.

General form of detection equation

Exactly the same detection equations can be derived for spectophotometric detection, refraction index detection or any other kind of detector.

Conductivity:

$$G_{\text{peak}} = (\text{CONST.})\,(\lambda_{S^-} - \lambda_{E^-})C_{S^-}$$

Spectrophotometric:

$$A_{\text{peak}} = (\text{CONST.})\,(\varepsilon_{S^-} - \varepsilon_{E^-})C_{S^-}.$$

Refractive index:

$$RI_{\text{peak}} = (\text{CONST.})\,(RI_{S^-} - RI_{E^-})C_{S^-}.$$

And the general equation for detector response is:

$$\text{SIGNAL}_{\text{peak}} = (\text{CONST.})\,(RF_S - RF_E)C_S$$

where RF is the response factor for the eluant and sample ions. The response factor can be for either anions or cations depending on whether anion exchange or cation exchange chromatography is performed. It can be seen from the general detection equation that the highest sensitivity results from the greatest difference in sample and eluant response factors. From a sensitivity standpoint, it does not matter if the eluant response factor is greater or smaller than the sample response factor. It just must be different. The relative magnitude of the eluant and sample response factor *does* affect the direction of the sample peaks. This is explained in the next section.

Direct and indirect detection

There are basically two types of sample peaks in ion chromatography. Peaks can be in either the positive (direct detection) or the negative direction (indirect detection). When peaks are in the positive direction, it is because the eluant ion has a very low detector response factor. Figure 2 shows an example of this behavior with conductivity detection. An "extreme" example of direct detection is with selective detectors. In this case the eluant detector response factor is essentially zero.

In indirect detection the eluant ion detector response factors are greater than the sample detector response factors. An example of this detection scheme is shown in Figure 3 for the conductivity detection of cations. Indirect detection has also been used extensively with spectrophotometric detectors (called indirect photometric IC) and with refractive index detectors. In fact most refractive index detection in ion chromatography is performed in the indirect mode. This is

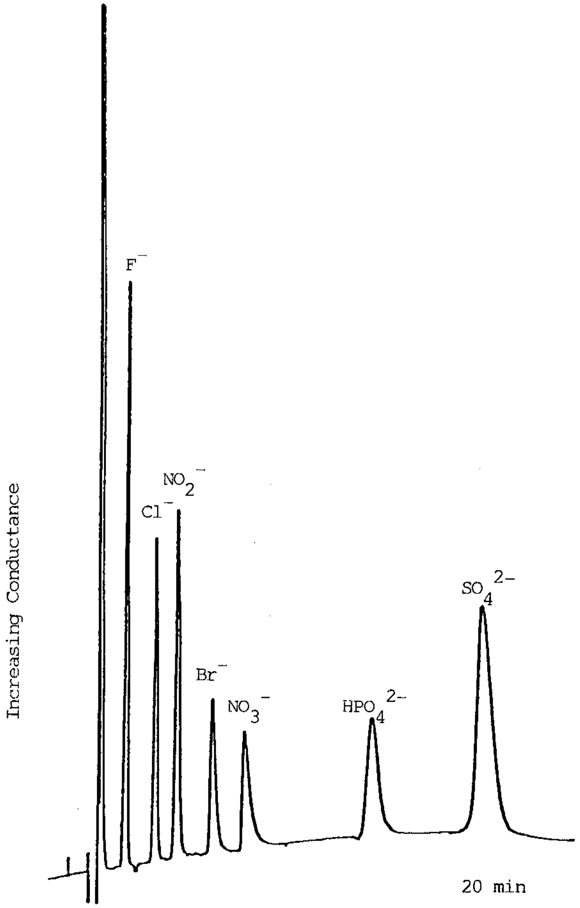

FIGURE 2 Separation of 10–20 ppm anion standard with 4 mM *p*-hydroxybenzoic acid, pH 8.5 eluant on a Wescan 269-029 Anion/R column with increasing conductivity detection. A system peak elutes at 25 minutes.

because the organic eluants normally used have a much higher refractive index than the inorganic sample ions. Conductivity detection can operate either as direct or indirect detection. Conductivity response factors for sample and eluant ions are shown in Table I.

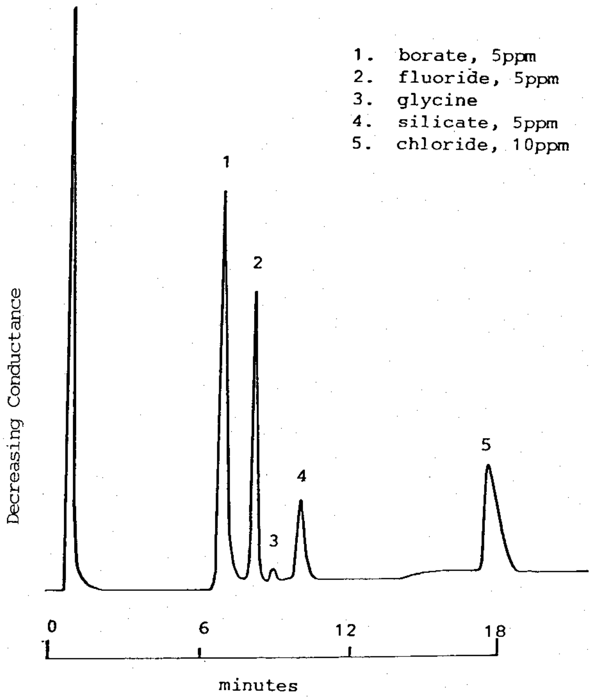

FIGURE 3 Separation of weak acid anions using 5 mM NaOH, 0.1 mM Na Benzoate eluant on a Wescan 269-029 Anion/R column with decreasing conductivity detection.

TABLE I

Relative equivalent conductances of eluant and sample ions

Ion type	Relative equivalent conductance
Hydroxide anion	200
Inorganic anions	60–70
Organic anions	30–40
Hydronium cation	350
Alkali metal cations	60–60

EFFECT OF ELUANT pH

There are several aspects of the effect of eluant pH on ion chromatography. The first is the ionization (or the partial- or non-ionization) of the sample ions. This affects the detection process indirectly because unless a sample ion is ionized it cannot exchange on the ion exchanger. A sample ion cannot be determined unless the ion is retained and separated by the column. A good example of this behavior is the separation of weak acid ions such as borate and silicate (Figure 4). In this case, a hydroxide eluant is used to separate the ions. But the high pH of the eluant also ionizes the anions so that they can be separated on the column. This scheme works very well because hydroxide ion happens to have a high equivalent conductance and the sample ions (which have a low equivalent conductance) are detected by conductivity detection.

In a similar way, a low pH eluant can be useful. Many samples, such as beverages and foods, contain a large amount of organic acids and ions. If one is interested in the inorganic ions then the problem is to "mask" the presence of these organic acids so that they do not interfere with the analysis. A good way to accomplish this is to use an acid eluant (for example 20 mM phthalic acid). The low pH of this eluant protonates the weak acid sample ions so that they pass quickly through the column with the solvent front. But the pH is not low enough to protonate the strong acid ions such as chloride, bromide, iodide, sulfate, etc. Thus these strong acid ions can easily be separated on the ion exchanger.

Besides affecting the form of the sample ions, the eluant pH can also affect the detector response of the sample ions. This is especially true for weak acid sample ions. The eluant and sample can exist in either the protonated or the unprotonated states:

Eluant: $HE \rightleftharpoons H^+ + E^-$

Sample: $HS \rightleftharpoons H^+ + S^-$.

And the ion-exchange reaction considering all states is as follows.

$$\begin{array}{cccc} \text{RESIN}-S+H^+ + E^- & & \text{RESIN}-E+H^+ + S^- & \\ \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright & \\ HE & & HS & \end{array}$$

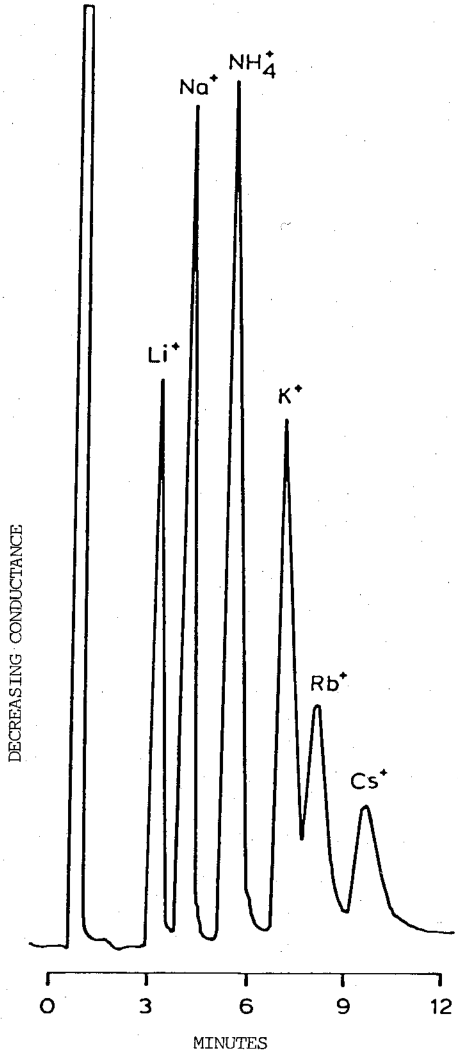

FIGURE 4 Separation of alkali metal and ammonium cation with a 1.0 mM nitric acid eluant on a low-capacity cation exchanger with decreasing conductivity detection.

If the sample ion is partially ionized it can still be separated on an ion exchanger, but the sensitivity for a particular ion is based on the contributions from the protonated and unprotonated forms. For example, when using a spectrophotometric detector, the molar absorptivity of an ion can shift with solution pH. The situation is even more dramatic for the conductivity detector. After all, a solution of a sample species can only conduct electricity if it is ionized. The general equation showing the effects of eluant and sample pH on conductance detection is shown below.

$$G_{\text{peak}} = (\text{CONST.})\,[(\lambda_{E^+} + \lambda_{S^-})I_S - (\lambda_{E^+} + \lambda_{E^-})I_E]\,C_S\cdot$$

I is the fraction of sample or eluant that is ionized.

ION EXCLUSION CHROMATOGRAPHY

It has been shown that the key to describing detector response in ion exchange chromatography is the fact that ion exchange is a replacement process. However, ion exclusion chromatography separations operate differently. The ion exclusion mechanism can be thought of as an addition process. The reasons for this can be explained by examining the separation and detection mechanisms.

Ion exclusion separation mechanism

Ion exclusion columns are packed with ion exchange resin. However, there are two major differences to the ion exchange material used for ion exclusion when it is compared to the material used for ion exchange. One difference is ion exclusion chromatographic columns have a much higher functional group capacity—up to 1000 times higher. The other difference is, in ion exclusion chromatography, a cation exchange resin (not an anion exchanger) is used to separate (weak acid) anions.

As the name implies, the ion-exchange resin acts as a semi-permeable membrane between the stationary and mobile phases in the column. Ionized sample solutes are excluded from the interior of the resin and pass quickly through the column. Non-ionic material (anions of weak acids) are not excluded from the resin phase. The materials partition and are separated on the column. Because the sample species are weak acid anions, the extent to which they are retained on the column depends on the eluant pH. Normally an acid eluant such as 0.002 N sulfuric acid is used (Figure 5).

As the separation is taking place, sample species are present in addition to the eluant species. There is no reduction in eluant concentration. Thus, although there may be a background signal, the detector response for a sample species is directly proportional to the sample response factor and the sample concentration.

Ion exclusion:

$$\text{Signal}_{\text{peak}} = (\text{Const.}) \quad RF \quad C_S.$$

Proof for this process is shown by Figure 5. The sulfuric acid eluant has a high equivalent conductance. The organic acid samples have low equivalent conductances. In spite of this the sample peaks are recorded as increasing conductivity peaks on top of the background signal from the sulfuric acid.

Eluant pH can also affect detection in ion exclusion chromatography. Normally a strong acid that is 100% ionized is used as the eluant. However, the sample acids are ionized to varying degrees depending on the eluant pH and the strength of the acid.

Ion exclusion equilibria:

$$\begin{array}{l} \text{RESIN}-HS+H^{+}+E \leftrightharpoons \text{RESIN}+HS+H^{+}+E^{-} \\ \qquad\qquad\qquad\qquad\qquad\quad \upharpoonleft\!\downharpoonright \\ \qquad\qquad\qquad\qquad\qquad\quad H^{+}+S^{-} \end{array}$$

Thus, the detector response equation for conductivity detection can be rewritten.

$$\text{Signal}_{\text{peak}} = (\text{Const.})\, \Lambda_S\, C_{S^-}.$$

Other detectors have been used for ion exclusion chromatography. The most successful is the UV spectrophotometric detector.[13]

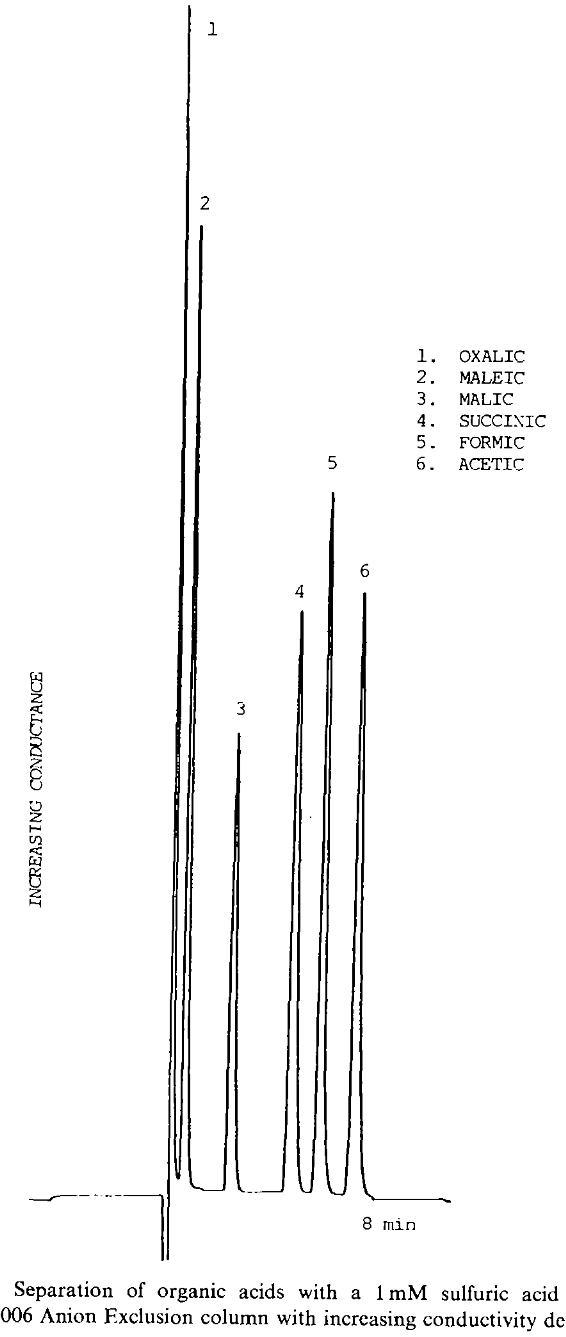

FIGURE 5 Separation of organic acids with a 1 mM sulfuric acid eluant on a Wescan 269-006 Anion Exclusion column with increasing conductivity detection.

CONCLUSIONS

Many different detectors have been used in single-column ion chromatography. These detectors can be operated either in the direct mode where the sample ions are monitored directly, or they can be operated in the indirect mode where the absence of the eluant ions is detected. The most popular detector for SCIC is conductivity. This detector can tolerate a wide range of eluant concentrations and changes in eluant pH. Depending on the eluant and separation column, separations of ions of weak acids, strong acids or mixtures of anions can be monitored. Conductivity detection has also been useful for cation detection.

Other detectors such as refractive index and spectrophotometric monitors can be used. Spectrophotometric detectors, especially, have been used for the direct and indirect detection of ions. Selective detectors such as the amperometric and detectors based on atomic absorption and emission can be useful when the analyst is interested in a particular type of ion.

Detector response equations are based primarily on the type of separation mechanism used to separate the ions. Equations for ion exchange detection are based on the fact that ion-exchange chromatography is a replacement process. Although ion-interaction chromatography is much more complicated and beyond the scope of this paper, the detection with this type of chromatography is similar to ion exchange. Ion-exclusion chromatography is an addition process. Detector response with this type of separation depends primarily on the detector response factor of the sample.

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