

ION CHROMATOGRAPHY
GENERAL REVIEW



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I. INTRODUCTION

Ion chromatography has become a widely used analytical technique for the determination of all types of ions. By using this technique, a wide range of ionic species in a single sample can be analysed without many analytical difficulties associated with the conventional methods, such as lengthy analysis time, labor-intensive procedures, limitation to one or two ions per sample, and sample matrix interferences.

Ion chromatography (IC) is an ion-exchange separation technique, using specialised columns and a suitable form of detection. The most widely used detector in IC is the conductivity detector. Temperature control for the column in IC uses conductivity as a detection mode is essential because the conductivity greatly depends on the temperature.

Other forms or modes of detection are UV absorption (including indirect absorption), refractive index, fluorescence, electrochemical (especially amperometric and pulsed amperometric), and postcolumn derivatization. A pulse-free flow of the mobile phase (eluant), which is necessary for both the sensitive UV and amperometric detectors, is ensured by a complex electronic control of the pump.

There are two groups of IC methods. The first group uses an ion-exchange column (separator column) and a second column (suppressor column). The suppressor column serves to chemically reduce the background conductivity of the eluant and, at the same time, converts the species of interest into a more conductive form. The second group uses only a low-capacity ion column and special eluants with low conductivity. **In this article, the principles of the latter IC will be shortly described.**

II. Basic principles

The chromatographic separation of ions requires ion exchange, the exchange of ions of like sign between a mobile (eluant) and a stationary phase (ion exchanger). The first requisite for the IC is the rapid transfer of analyte ions between the stationary and the mobile phase. To fasten the exchange, special surface-functional materials were developed such as polymeric and silica-based ion exchangers (Walton, 1995).

An equation can be derived for the elution volume (or retention volume) of a

small amount of analyte ions injected into a flowing eluant stream at the head of an ion exchange column. Consider a simple case, the injection of a trace of anion A^- into a stream of a dilute base MOH, flowing through a column packed with an anion exchange resin (Res-OH). Ion exchange takes place according to the reversible reaction :



The equilibrium constant of this reaction is given by :

$$K = \frac{[\text{Res-A}][\text{OH}^-]}{[\text{Res-OH}][A^-]}$$

If the concentration of hydroxide ions in the flowing eluant is $[\text{OH}^-]$, and the total ionic capacity of the column (the quantity of exchangeable ions in the stationary phase) is C, then nearly all the exchangeable ions are hydroxide ions.

$$V_e = V_i + KC/[\text{OH}^-]$$

where V_e and V_i are respectively the elution or retention volume of the anion A^- and the void volume of the column.

This equation shows that if the capacity of the exchanger is lowered by using a surface-functional exchanger, the concentration of the eluant must also be lowered. Low capacity exchanger requires dilute eluants, which make detection by conductivity easier. When high-capacity ion exchangers (gel-type resins) are used, the eluant concentration are so high (between 0.1 M and 1 M or more), so that the changes in conductivity caused by the analyte ions are practically undetectable. Thus, the only hope of detecting and measuring the conductivity changes lies in using very dilute eluant, which in turn require ion exchangers of low capacity.

When the solution of salt MA is introduced at the head of an anion exchange column into a flowing solution of MOH, anions A^- enter the exchanger, move back and forth between the exchanger and the solution, and eventually come out in the effluent, taking place of ions OH^- . The concentration of ions M^+ in the flowing solution remains constant. If, ions OH^- conduct better than A^- the conductivity falls as ions A^- emerge and vice versa. The altering in conductivity can be measured to result in analytical estimation of the anion in the sample.

III. Technique and instrumentation of non-suppressed IC

An instrument layout of the IC components is shown in figure 1.

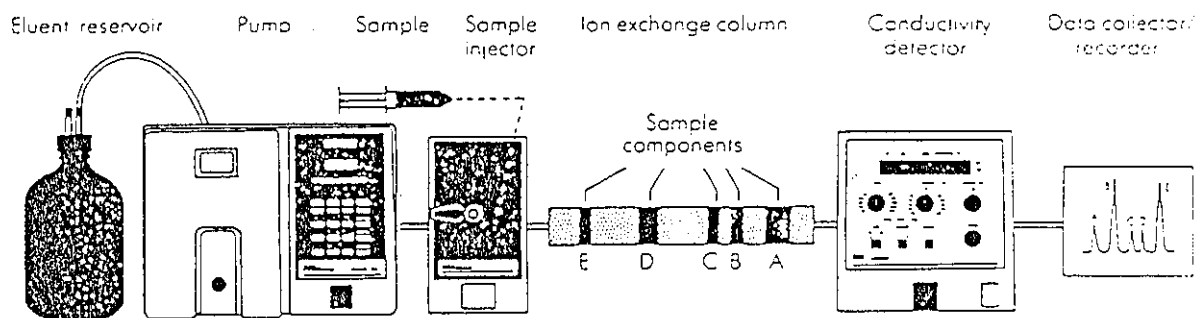


Figure 1. Instrument layout of IC

A sample in a liquid state is injected into the system and carried through the column by the eluant at a fixed flow rate. Within the column the ionic species exhibit varying degrees of attraction for the resin material and migrate through the column at different rates. After separation the ions are carried by the eluant into a detector which responds to the amount of each component. Each component is identified by the retention time (which can be determined by using known ions) and quantitatively estimated by the magnitude of the response (area or peak height).

The most important part of the chromatography is the analytical column (Weiss, Handbook of IC). The selection of a suitable stationary phase and the appropriate chromatographic parameters determines the quality of the analysis. The column bodies are made of inert materials and are generally operated at room temperature.

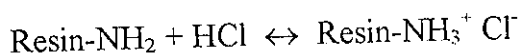
IV. Types of ion exchange materials

Cation-exchange resins are classified into strong acid and weak acid types. The first group retains the negative charge on the fixed ion over a wide pH range, whereas the second group is ionised only over a much narrower pH range. The weak acid type requires a sufficiently high pH for use, and this is exemplified by the use of a NaOH eluant with a carboxylic acid cation-exchanger.



Similarly, the anion-exchangers are classified as strong base and weak base

exchangers. Quaternary amine functional groups form strong base exchangers, while less substituted amines form weak base exchangers. A weak base material will function only when the pH is sufficiently low to protonate the nitrogen atom in the functional group.

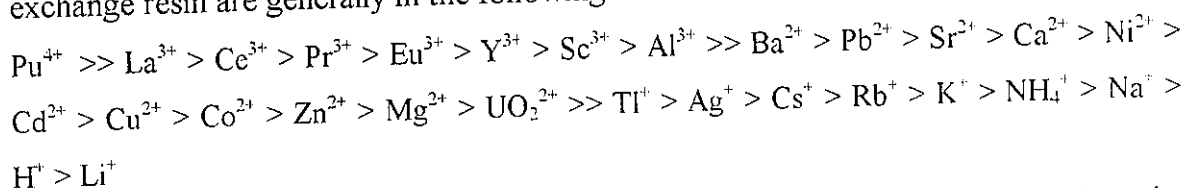


The ion-exchange capacity of an ion-exchanger is determined by the number of functional groups per unit weight of the resin. It plays a large role in determining the concentration of competing ion used in an eluant to be employed with that resin.

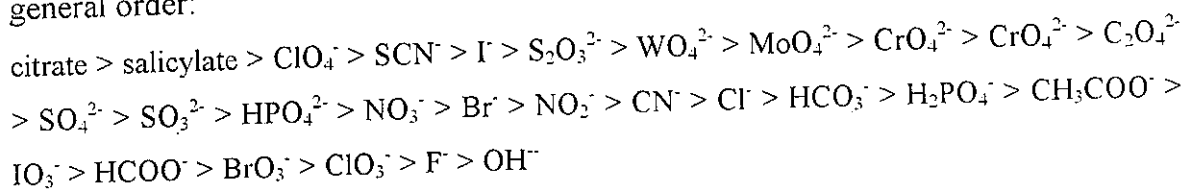
Table 1. Functional groups in some typical synthetic ion-exchange materials (Haddad & Jackson, 1990)

Cation Exchangers		Anion Exchanger	
Type	Functional Group	Type	Functional Group
Sulfonic acid	$-\text{SO}_3^- \text{H}^+$	Quaternary amine	$-\text{N}(\text{CH}_3)_3^+ \text{OH}^-$
Carboxylic acid	$-\text{COO}^- \text{H}^+$	Quaternary amine	$-\text{N}(\text{CH}_3)_2(\text{EtOH})^+ \text{OH}^-$
Phosphonic acid	$-\text{PO}_3\text{H}^- \text{H}^+$	Tertiary amine	$-\text{N}(\text{CH}_3)_2^+ \text{OH}^-$
Phosphinic acid	$-\text{PO}_2\text{H}^- \text{H}^+$	Secondary amine	$-\text{N}(\text{CH}_3)^+ \text{OH}^-$
Phenolic	$-\text{O}^- \text{H}^+$	Primary amine	$-\text{NH}_3^+ \text{OH}^-$
Arsonic acid	$-\text{AsO}_3\text{H}^- \text{H}^+$		
Selenonic acid	$-\text{SeO}_3^- \text{H}^+$		

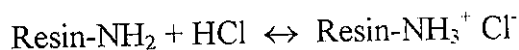
Selectivity coefficients for the uptake of cations by a strong acid cation-exchange resin are generally in the following order:



Selectivity coefficients for anions on strong base anion exchangers follow the general order:



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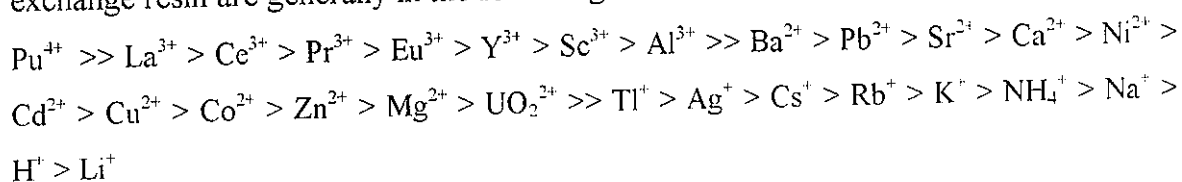


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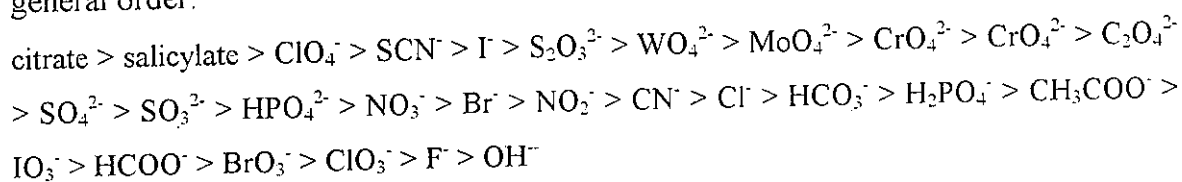
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V. Eluant for non-suppressed IC

The role of an eluent in an ion exchange separation is to compete with solute ions for the fixed ions on the stationary phase and to separate the mixture of solute ions into well-defined bands. The detection mode to be used in an ion chromatograph is the major factor that determines the types of eluants that are suitable for a desired separation.

The eluant pH is a vital parameter in determining the characteristics of the eluant, and influences the charges on both the eluant and solute ions. These effects are particularly important in anion separations, where they play a large part in governing solute retention.

The ability of eluant species to form complexes with solute (usually metal) ions or sample components is often highly desirable and so the complexation characteristic of the eluant may sometimes be of importance.

The eluant concentrations used in non-suppressed detection are usually below 0.01 M, and are often around 0.001 M. They must be matched to the capacity of the exchanger, which is commonly about 10 microequivalents per gram.

For the chromatography of anions, common eluants are benzoate, phthalate, and salicylate. The equivalent conductances of these ions are low, therefore the conductivity of the effluent rises as inorganic anions emerge. Another favoured eluant for anion chromatography is a solution containing boric acid and a polyol, gluconic acid. These substances combine to give acids that are stronger than boric acid. At pH 8.5, the usual pH for borate-gluconate eluant, most of the acids are ionized and the eluting power is adequate. The conductivity of this eluant is low, and rises when other anions are eluted.

Sodium or potassium hydroxide is occasionally used as eluant in non-suppressed chromatography. The hydroxide ion has a high conductivity, so that the conductivity falls when other anions are eluted.

VI. IC detectors

The function of the detector is to monitor the column effluent and provide a means of detecting solutes. The choice of detector is often determined by the chemical characteristics of the analyte species and this choice may subsequently determine which

eluant, which stationary phase and mode of chromatography should be used. The detector response will be related to the amount of the analyte in the column effluent through different analytes will respond to differing extents and hence the detector must be calibrated with respect to each of the analytical species of interest. An ideal detector for liquid chromatography should have high sensitivity, good stability and reproducibility, linear response over several orders of magnitude, and high reliability and ease of use.

Table 2. Characteristic of Chromatographic Detectors
(Braithwaite & Smith, 1996)

Detector	Detection limit	Linear range
Ultraviolet (absorbance)	$5 \times 10^{-10} \text{ g.cm}^{-3}$	$10^4 \sim 10^5$
Photo-diode (absorbance)	$> 2 \times 10^{-10}$	$10^4 \sim 10^5$
Infra red (absorbance)	10^{-6}	$\sim 10^3$
Refractive Index (RIU)	5×10^{-7}	$10^3 \sim 10^4$
Conductimetric	10^{-8}	$10^3 \sim 10^4$
Mass Spectrometry	10^{-10}	10^4

The detector that is commonly used in an ion chromatograph is conductivity detector. Since the materials to be separated are in the form of ions, a continuous record of the electrical conductivity of the effluent can be used to detect the eluting species.

Any other methods of detection used in liquid chromatography can be used in ion chromatography (Walton, 1995), though some are more useful than others. Common means of detection in IC are : UV absorption (including indirect absorption), electrochemical (especially amperometric and pulsed amperometric), and postcolumn derivatization.

UV absorption detector

Most simple inorganic cations and anions are transparent in the UV, but the larger, more polarizable anions absorb UV radiation, absorbing more strongly at shorter wavelength. Absorbances at 200 – 210 nm are sufficiently strong to detect bromide, iodide, nitrate, nitrite, thiocyanate, thiosulphate, and chromate. Carboxylate ions absorb satisfactorily below 215 nm. (Walton, 1995).

DAFTAR PUSTAKA

1. Joachim Weiss, *Handbook of Ion Chromatography*.
2. Skoog, D.A., West, D.M., *Fundamentals of Analytical Chemistry*.