1. INTRODUCTION

1.1 Anions and Cations Analysis in Geological Materials

During the past 40 years there has been an enormous increase of interest in the role played by elements present in low concentration in geological and biological systems. The growth of research in these fields owes a great deal to the development and improvement of methods of chemical analysis in this period. In fact, many of the advances in analytical techniques and instrumentation have been stimulated by the special requirements of fields as diverse as geochemistry, mineral exploration, soil science, agriculture and horticulture, environmental science, clinical science, toxicology, forensic science and archaeology. These special requirements have included the determination of large numbers of elements at trace or ultratrace levels, the use of very small samples, and the processing of very large numbers of samples in a short time.

A knowledge of trace-element concentrations in geological materials [1] such as minerals, rocks, ores, soils, sediments, coals and fresh and saline waters is important in a number of scientific fields. The first of these is geochemistry itself, the progress of which has always relied heavily on developments in chemical analysis. Geochemistry is primarily concerned with elucidating the behavior of the chemical elements through the natural processes occurring in the earth and in extraterrestrial bodies.

The collection of data on the abundance of elements in various rock types is therefore fundamental to the development of theories of distribution and migration and can provide clues about the nature of the physical and chemical environment of the rock throughout its geological history. For many purposes, the study of trace elements is more rewarding than that of macroconstituents, because their

concentrations can range over several orders of magnitude, compared with perhaps a factor of three or four for the macroconstituents.

In the field of mineral exploration the development of rapid instrumental methods for multielement trace analysis has facilitated surveys of rock sample, stream sediments, soils and vegetation on an unprecedented scale. In soil science, agriculture and horticulture, interest in trace elements has been stimulated by the discovery of the role of several essential elements in plant and animal nutrition. It has also been possible to establish the part played by deficiencies or excesses of certain elements in contributing to disorders of plants, animals and humans. In archaeological investigations trace analysis can help to indicate the origin of materials such as pottery fragments, metal implements, ornaments and artifacts made from stone or volcanic glass.

Ion chromatography is a versatile, selective and sensitive method for the variety of anions and cations at trace and ultratrace levels. It has been applied to hundreds of problems in various fields involving ionic analysis in clinical, food, pharmaceutical, industrial plating solution and environmental samples [2] .

Ion chromatography has been employed in the determination of anions and cations in geological materials. The anions investigated are usually fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate. The cations investigated are iron, zinc, manganese, copper and cobalt. The detector system is based on conductometric and UV/vis spectrophotometric measurement, the latter being an indirect detector or post column reaction type.

1.2 Ion Chromatography (IC)

Ion chromatography has become a very sensitive and efficient analytical technique for the determination of inorganic cations and anions since its introduction by Small *et al.* In 1975 [3]. The original technique was developed to measure either cations or anions using ion-exchange resins and a suppressor column to increase the sensitivity of detection. By removal of the suppressor column and use of an eluent with low conductance, Gjerde *et al.* [4] accomplished the separation and detection of ions using a non-suppressed ion chromatographic technique. Through the use of various complexing agents in the eluent, Sevenich and Fritz [5] accomplished the separation of divalent transition metal cations with conductivity detection.

The concept of ion chromatography has allowed the analysis of a wide variety of samples with minimum, or at least reduced, sample preparation. Today the chromatographic analysis of ionic materials is widely applied and rapidly expanding.

The number of species that may be determined continues to grow, as does the number of areas of science and technology where ion chromatography plays an important role. **Table 1.1** gives some idea of the breadth of application of ion chromatography at the present time.

Table 1.1 Types of samples analyzed by ion chromatography [6]

Acid rain	Ore
Analgesics	Pesticides
Chemicals	Pharmaceuticals
Detergents	Physiological fluids
Drinking water	Plating baths
Fermentation broths	Protein hydrolyses
Fertilizers	Pulping liquors
Foods and beverages	Soil and plant extracts
High-purity water	Waste water

Classification of Ion Exchangers

Ion exchangers are divided into groups depending on the strength of the conjugate acid or base of the functional group, as shown in **Table 1.2**

Table 1.2 Chemical classification of ion exchanger resins [7]

Ion exchanger	Type	Active group
Cation exchanger	Strongly acidic	Sulphonic acid
	Moderately acidic	Carboxylic acid
	Weakly acidic	Phosphoric acid
Anion exchanger	Strongly basic	Quaternary ammonium
	Moderately basic	Secondary amine
	Weakly basic	Tertiary amine (aromatic and aliphatic matrix)

Ion exchangers are the most widely used stationary phase in IC. An ion exchanger comprises three important elements: an insoluble matrix, which may be organic or inorganic; fixed ionic sites, either attached or an integral part of the matrix; and associated with these fixed sites, an equivalent amount of ions of charge opposite to that of the fixed sites. The attached groups are often referred to as functional groups. The associated ions are called the counter ions [6].

The separator column separates the sample anions by adsorption and ion exchange phenomena and then the suppressor column converts the anion into completely dissociated mineral acid with a high conductivity. Meanwhile, the suppressor column is continuously converting the eluent anion into a slightly dissociated weak acid with a low conductivity.

1.3 Instrumental

Ion chromatography uses the principle of high performance liquid chromatography (HPLC). The ion chromatography was developed to solve several specific analytical problems in aqueous systems.

The components of the ion chromatograph performing functions identical to those of any liquid chromatograph are shown in **Figure 1.1**. There are five major components in a suppressor type in the chromatograph.

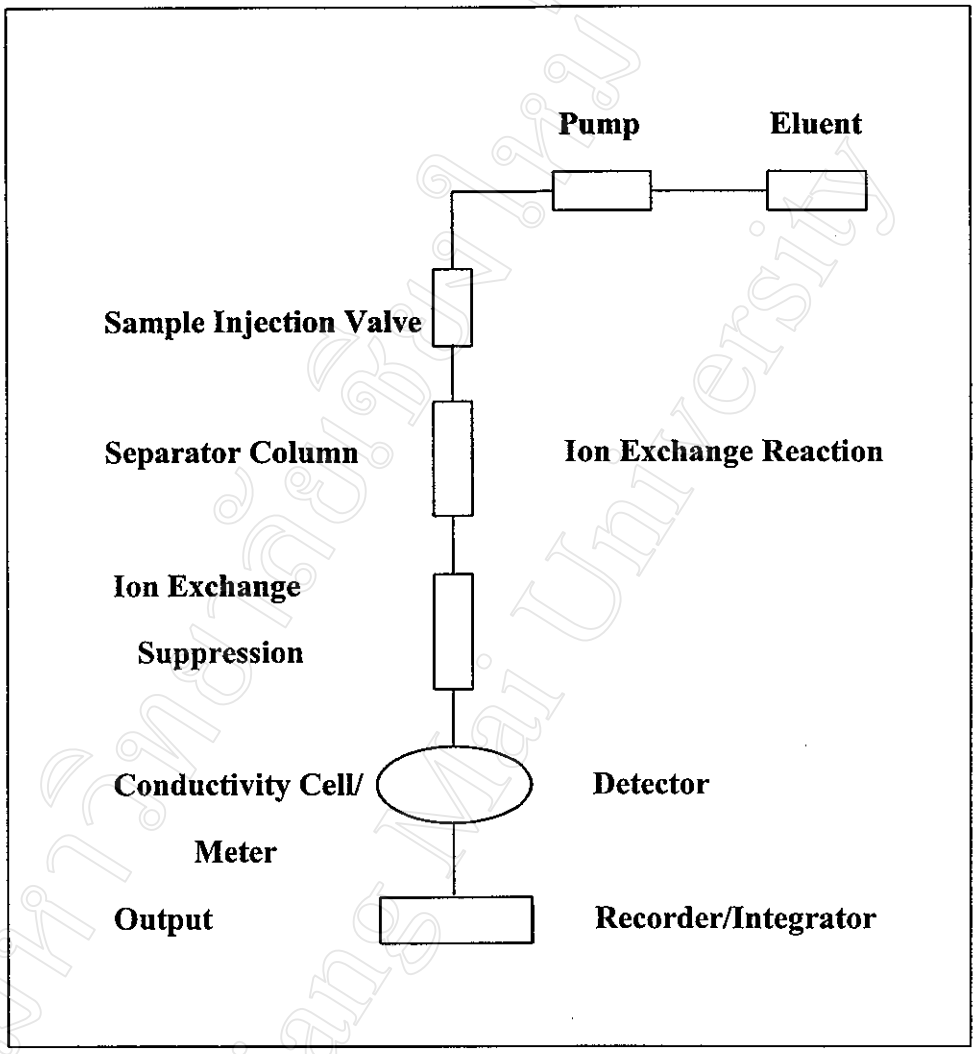

Figure 1.1 Schematic of a dual ion chromatographic system [7]

Each of these components is discussed separately. The eluent is pumped through the injection system into the separating column. The sample to be analysed is injected into the eluent via an injection loop. The sample passes through the separating column. Anions are separated using a low-capacity anion exchanger because it lowers elution times and it permits lowering of eluent concentrations, which in turn can have directly beneficial effects on the sensitivity of detection and it also tends to improve mass transfer rates because of the reduced diffusion distance in the resin phase. The ions separated in the column and carried by the eluent are introduced into the suppressor system and then the detector. The suppressor type ion chromatography has unique detector in that a second ion-exchange column is an integral part of the detector. This column, called the suppressor column, is used in series between the separating column and flow through conductivity cell.

The anion self-regenerating suppressor[8] requires a constant water feed through the regenerant chamber to achieve suppression. Water can be delivered to the suppressor regenerant chambers either from recycled eluent in the auto-suppression recycle mode of operation or with deionized water from a separate pressurized bottle in the auto suppression external mode of operation.

As for the suppressor column, the first type is anion self-regenerating suppressor, as shown in **Figure 1.2**.

The water regenerant undergoes electrolysis to form hydrogen gas and hydroxide ions in the cathode chamber while oxygen gas and hydronium ions are formed in the anode chamber. Cation exchange membranes allow hydronium ions to move form the anode chamber into the eluent chamber to neutralize hydroxide. Sodium ions in the eluent, attracted by the electrical potential applied to the cathode, move across the membrane into the cathode chamber to maintain electric neutrality with the hydroxide ions at the electrode.

The second type of the suppressor column is cation self-regenerating suppressor [9] which can also be used in the chemical suppression mode utilizing tetrabutylammonium hydroxide as a chemical regenerant instead of using an applied current and deionized water, as shown in **Figure1.3**. Chemical suppression with the cation self-regenerating suppressor is a neutralization reaction and selective desalting process carried out across the cation exchange membranes and combine with the acidic eluent cation, in this case hydronium ion, to form water. At the same time, eluent anions move across the membranes into the regenerant stream replacing the hydroxide ions.

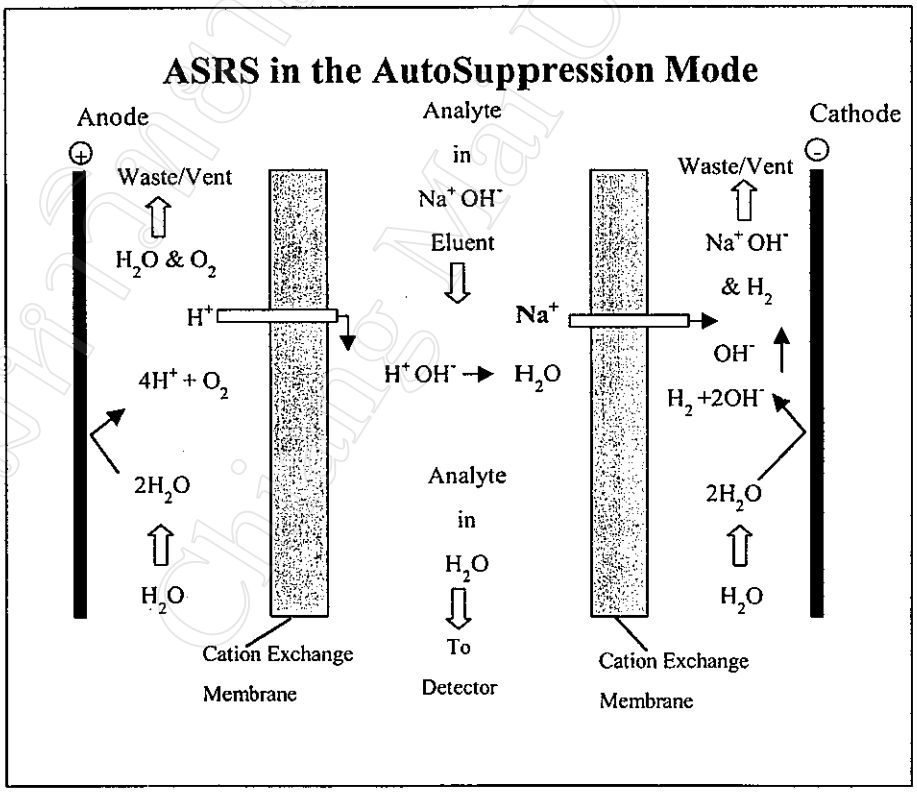

Figure 1.2 Auto suppression with the anion self-regenerating suppressor (ARSR) [8]

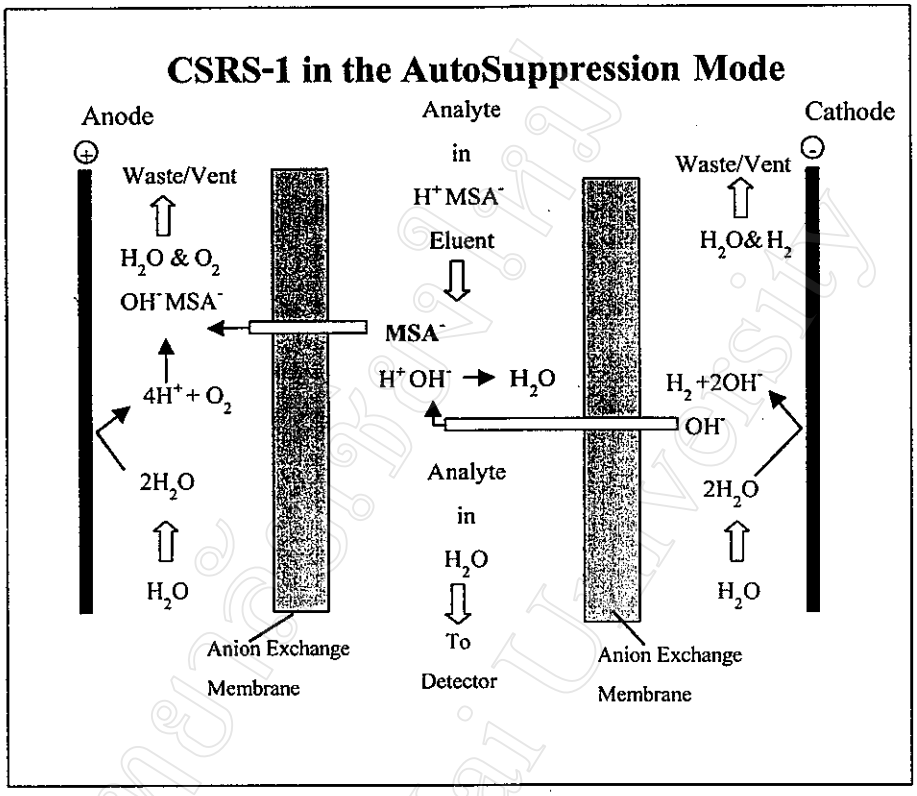

Figure 1.3 Chemical suppression with the cation self-regenerating suppressor (CSRS-1) [9]

1.4 Detectors

Ion chromatography is a form of high-performance liquid chromatography (HPLC). Its true definition is a matter of debate. A good definition is that ion chromatography is simply the liquid chromatography of ions, implying that any HPLC separation and detection method can be used and still be called ion chromatography. Regardless of which definition one accepts, ion chromatography is clearly more than just ion-exchange chromatography with conductometric detection. All the detectors commonly used in HPLC are now used in ion chromatography. Although the conductivity detector is probably the most popular, other forms of detection each have specific advantages for different types of analyst.

In line detector are used for automatic identification of ions after their separation on a chromatographic column. The following are properties of a good IC detector : high sensitivity, small cell volume, linear relationship, stable background, short time response, stability with respect to flow rate and temperature.

The main detection methods which have proven to be useful can be classified as either electrochemical or optical detection.

1.4.1 Conductometric detector [6]

Conductometric detection, at one time relatively neglected, is now one of the major detection methods in the chromatographic analysis of ionic species. As a means of detection, conductance monitoring has a number of features to recommend :

- Electrical conductivity is a universal property of ionic solutions.
- At the low concentrations typical of chromatography, conductivity is proportional to concentration.
- The detector, by virtue of its simplicity, is robust and capable of prolonged trouble-free operation.
- Since the cell is amenable to virtually limitless miniaturization, any inefficiency attributable to detector cell volume can be easily eliminated

The conductivity of a solution is measured by applying an alternating or pulse potentials between two electrodes in a conductivity cell. Negatively charged ions migrate to the anode and positive charged ions migrate to the cathode. A conductor is a material that contains a mobile charge carrier. Of course, the electrons in metals make conductors, but there are ionic conductors too. Ionizable species dissolved in polar liquid conduct electricity because the ions are mobile. One can measure the conductance of a sample by measuring current across the conductor at some applied voltage difference. The conductance of a solution, which is the reciprocal of electric resistance, R, is measured in reciprocal ohms (mhos), also called siemens(S).

The conductivity of a dilute solution is the sum of the individual contributors to conductivity of all ions multiplied by their concentrations. That is, conductivity is proportional to concentration followed by Kohlrausch's law of independent migration [10] :

$$K = \sum_i \lambda_i \, Ci/1000 \qquad \text{.....(1.1)}$$

K = measured concentration in S/cm

λ_i = ionic limiting equivalent conductivity

C_i = concentration of ions in equivalent/litre

Table 1.3 Equivalent conductivities (λ°) in aqueous solution, at 25 °C (S ·cm^2/equiv) [10].

Anion	λ°	Cation	λ°
OH^-	198	H^+	350
F^-	54	Li^+	39
Cl^-	76	Na^+	50
Br^-	78	K^+	74
I^-	77	NH_4^+	73
NO_3^-	71	Mg^{2+}	53
HCO_3^-	45	Ca^{2+}	60
SO_4^{2-}	80	Sr^{2+}	59
$Acetate^-$	41	$CH_3NH_3^+$	58
$Benzoate^-$	32	$N(CH_3CH_2)_4^+$	33

1.4.2 Spectrophotometric detectors [6]

Spectrophotometric detectors are common in HPLC. Their detection can be classified as two types as in the following.

1) Direct detection

Direct spectrophotometric detection can only be used when the analyte absorbs usually by UV or visible light. These detectors are useful for organic ions, particularly aromatic compounds. Inorganic anions can also be

determined spectrophotometrically. For nitrate, nitrite and bromide selectivity and sensitivity is superior.

2) Indirect detection or post column reaction

This method is used to determine ions for which the spectroscopic absorption is less than the eluting ion. The analyte ions are converted into strongly absorbing coloured compounds. This is achieved by adding a spectrophotometric reagent to the eluent after it passes through the separating column. The coloured complex then passes through the detector. The post column reaction must be fast.

1.5 Theoretical principle

The separation of substrate in ion chromatography is based on ion exchange and an equivalent exchange of solution ions for solid phase ions. The extent of separation of the peaks is measured by resolution (R_s) which is equal to the ratio of the distance between the peak maxima, Δt_R ,to the mean band width of the two neighboring peaks, w [6] :

$$R_s = t_R / \overline{w} = 2(t_{R2} - t_{R1})/(w_{b1} + w_{b2}) \quad \text{.....(1.2)}$$

whereas $t_{R2} > t_{R1}$

where t_{R1} and t_{R2} are the retention time w_{b1} and w_{b2} are the peak width measured by the baseline intercept as shown in **Figure1.4**. Peaks are considered to be fully resolved when R_s = 1.5 when their separation is 99.7 % complete. In most practical cases, however, R_s = 1.0 corresponding to 98% separation is usually adequate [11] .

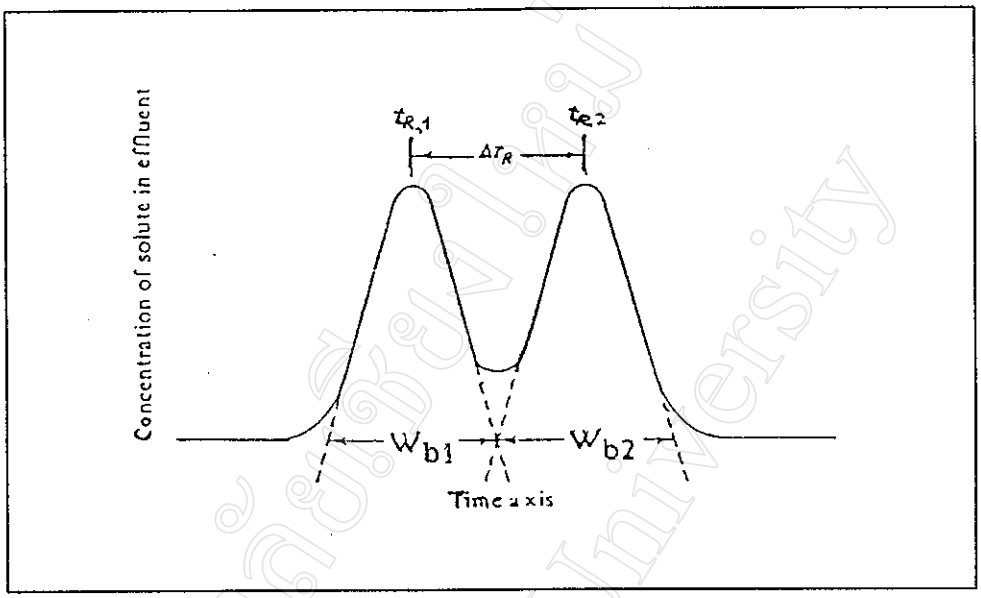

Figure1.4 Chromatogram of two components used in the definition of resolution.

The resolution is a basic measure of efficiency of the chromatographic system in separating the two components.

Column efficiency can be expressed by the approaches of chromatographic theory. A dimensionless measure of column efficiency, N, is called the plate number or number of theoretical plates. A large plate number signifies that the relative band spreading is small and that the chromatographic system is highly efficient. These values allow us to express the number of theoretical plates [12] as given in **Equation 1.3** .

$$N = 16(t_R / w_{1/2}) = 5.54\ (t_R / w_{1/2}) \quad \text{.....(1.3)}$$

where t_R is the retention time of solute, $w_{1/2}$ is the base peak width and w is the width at half-height, as shown in **Figure 1.5.**

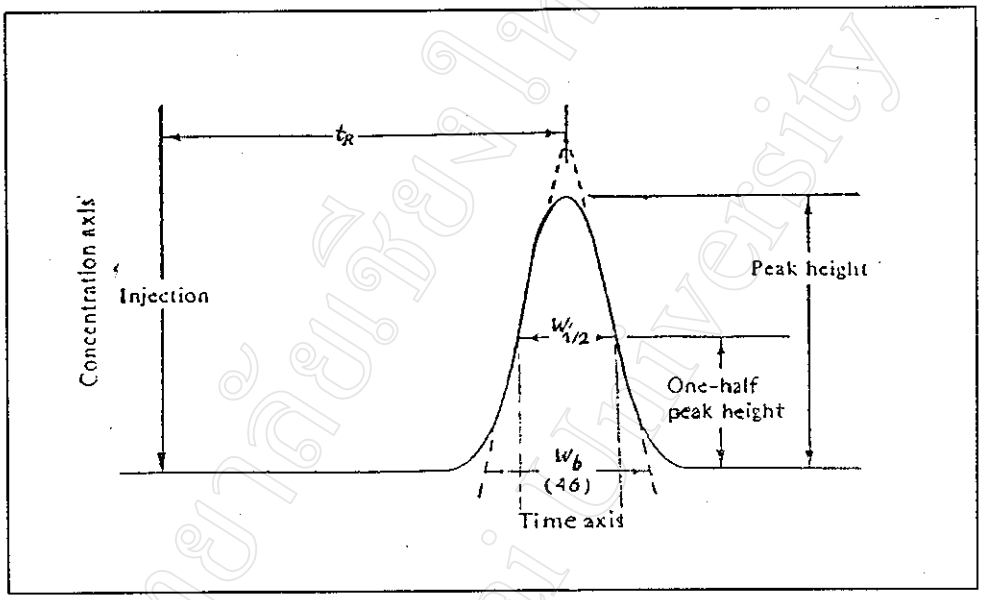

Figure 1.5 Evaluation of a chromatographic peak for column efficiency.

The height equivalent to a theoretical plate (H) as thickness of theoretical plate is expressed by

$$H = L/N \qquad \text{.....(1.4)}$$

where L is the column length in mm or cm.

The rate theory is based on the rate of mass transfer between two phases, diffusion rate of solute along the column, eluent flow rate and hydrodynamics of mobile phase. Therefore, factors may be concluded and shown as the relationship

between column efficiency and variable in column composition and analytical conditions, as expressed by the Van Deemter equation [13] :

$$H = A + B/u + Cu \qquad \text{.....(1.5)}$$

where A = eddy diffussion term

B/u= longitudinal diffusion term

Cu = mass transfer term

1.6 Anions and Cations by Ion Chromatography

Early publications of ion chromatography work described environmental applications. Since it was introduced in 1975, much of the practice of it has been well-established science transformed into easily practiced technology. Several books and general review articles have been published on ion chromatography in recent years. Ion chromatography has been widely used for the determination of ions in geological material.

Table 1.4 Research of the determination of ions in geological materials by IC.

Researcher	Analyte	Type of sample	Technique	Reference
Evans *et al.*	F^-,Cl^-,SO_4^{2-}	Rock	Pyrohydrolytic-IC	14
Cox and Saari	Cl^-	Coal	Solvent extraction	15
Sallings *et al.*	S	Rock, Soil	Na_2O_2 Fusion	16
Conrad and Brownlee	F^-	Coal, Ash and Other geological materials	Hydropyrolytic-IC	17
Cox *et al.*	Cl^-, PO_4^{3-},SO_4^{2-}	Sugar, Coal and Surface water	Carbonate fusion and Donnan dialysis	18
Petric *et al.*	SO_2, SO_4^{2-}, $S_2O_6^{2-}$	Mineral leachates	-	19
Shotyle	Cl^-,NO_2^-,Br^-,NO_3^-, HPO_4^{2-},SO_4^{2-} and Oxalate	Organic-rich natural water	-	20
Shotyle and Steinmann	F^-, acetate, formate, HCO_3^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, $S_2O_3^{2-}$, Na^+, K^+, Mg^{2+}, Ca^{2+}	Organic-rich natural water	-	21

Table 1.4 Research of the determination of ions in geological materials by IC (Cont.).

Researcher	Analyte	Type of sample	Technique	Reference
Moran *et al.*	I^-	Geological materials	Extraction	22
Schnetger and Muramatsu	I^-, Br^-, Cl^-,F^-	Geological and Biological materials	Pyrohydrolysis	23
Jones and Tarter	Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Cl^-, SO_4^{2-}, NO_3^-	Samples of widely varying composition; example hair samples	Single detector system and dual detection system	24
Siriraks and Kingston	Transition elements	Environmental and Biological samples	Chelation IC	25
Kanai	Fe^{2+}, Fe^{3+}	Rock	Post column	26

In this work, suppressed ion chromatography was used for simultaneous determinations of anions and cations of the author's interest such as F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Fe^{3+}, Cu^{2+}, Zn^{2+}, $Co^{2+}$and Mn^{2+}. Suppression mode was necessary in this work when detection was made on a conductivity detector, a universal detector capable of detecting and substance with appreciable conductivity. As for the post column mode, suppression of interferences was not required because the UV/vis detector used at any suitable wavelength would be relatively more selective.

1.7 The Scope and Aim of This Research

The chromatographic condition of two systems of ion chromatography, namely a suppressed ion chromatography and post column derivatization were optimized for determination of anions and cations. The obtained conditions were applied to determine the amounts of anions and cations in geological materials such as hot spring waters, rain waters, and coals. The obtained results were quantitatively compared with data obtained from the spectrophotometric (UV/vis), the ion selective electrode (ISE), the atomic absorption spectrophotometric (AAS) and the inductively coupled plasma spectrophotometric (ICP) technique.

The aims of this research are as follows.

1) To investigate and obtain optimum ion chromatographic conditions for determination of ions of interest, including F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+}.

2) To apply the conditions obtained to the analysis of anions and cations in some hot spring waters, river water, rain waters and coal samples in the north of Thailand.

3) To compare results from the ion chromatographic technique with those from spectrophotometric (UV/vis), the ion selective electrode (ISE), the atomic absorption spectrophotometric (AAS), and inductively coupled plasma spectrophotometric (ICP) techniques.