1. Introduction

1.1 Anions and Cations Analysis

Water is the lifeblood of the ecosphere. Despite its importance, water is the most poorly managed resource on Earth. Clean water is not all that readily available in many countries, including Thailand. As sources of potable water are limited, bottled drinking water commercially produced by various water purification plants is quite a common scene in Thailand. Many factories seem to be unaware of the standards for drinking water stipulated by the Ministry of Public Health [1]. The quality of drinking water is thus questionable. In Chiang Mai, certain people still drink water obtained from wells. Such water often lacks necessary data to establish whether or not it is fit for drinking. Even when there is some information about it, it is usually related to heavy metals or cations and data on anions is hardly found.

Ion chromatography is a versatile, selective and sensitive method for the variety of anions and cations at trace and ultra trace 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 potable drinking water and well water. The anions investigated are usually fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate. The cations investigated are calcium, magnesium, nickel, zinc, lead, manganese and strontium. 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

Ion chromatography was first introduced in 1975 by Small and his co-workers [3]. Classical methods of separation and quantitative determination of anions and cations in aqueous solutions generally require different reagents. A dual column system permits the seperation and determination of various ions in a short period of time. The initial system utilizes a low-capacity anion-exchange column and it is followed by a high capacity, hydrogen form, cation-exchange column [4].

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.

Table 1.1 Chemical classification of ion-exchange resins [5].

Ion exchanger	Type	Active group
cation exchanger	strong acid	sulfonic acid
	weak acid	carboxylic acid
	weak acid	phosphoric acid
anion exchanger	strong base	quaternary ammonium
	weak base	secondary amine
	weak base	tertiary amine (aromatic matrix)
	weak base	tertiary amine (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 associated ions are called the counterions.

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.

1.2.1 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 an 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 [5].

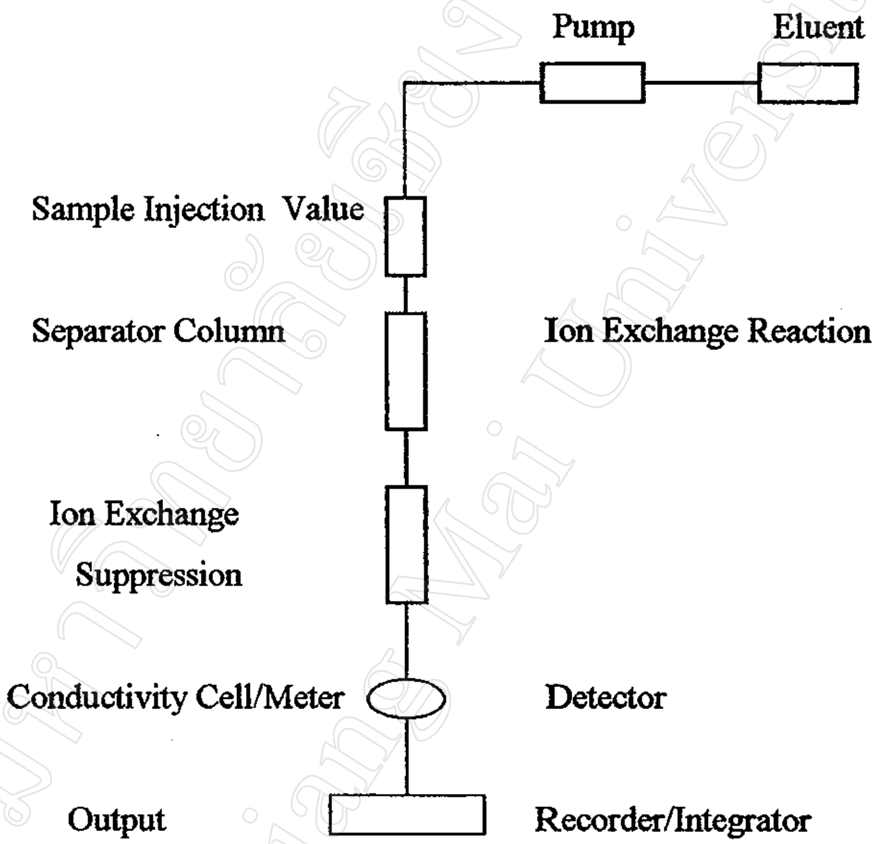

Figure 1.1 Schematic of a dual ion chromatographic system

Each of these components is discussed separately. The eluent is pumped under 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. 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 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** [6].

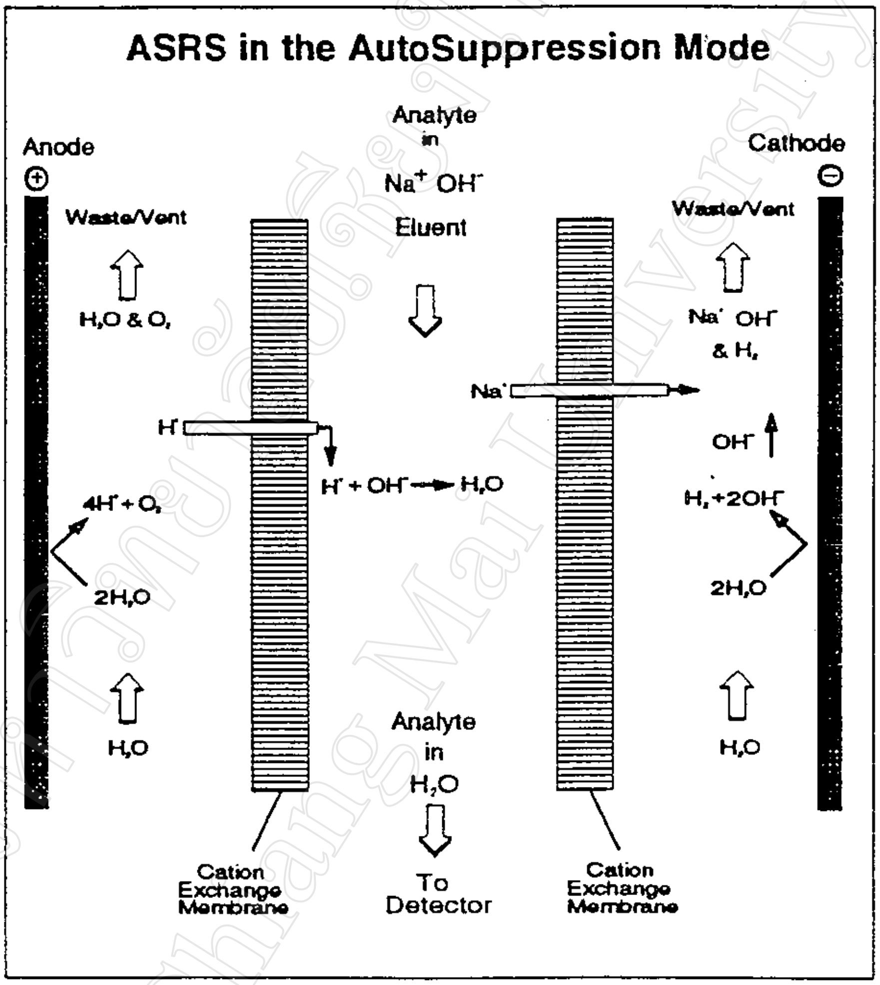

Figure 1.2 Auto suppression with the anion self-regenerating suppressor (ARSR-1).

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 electronic neutrality with the hydroxide ions at the electrode.

The second type of the suppressor column is cation self-regenerating suppressor [7] 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 **Figure 1.3**.

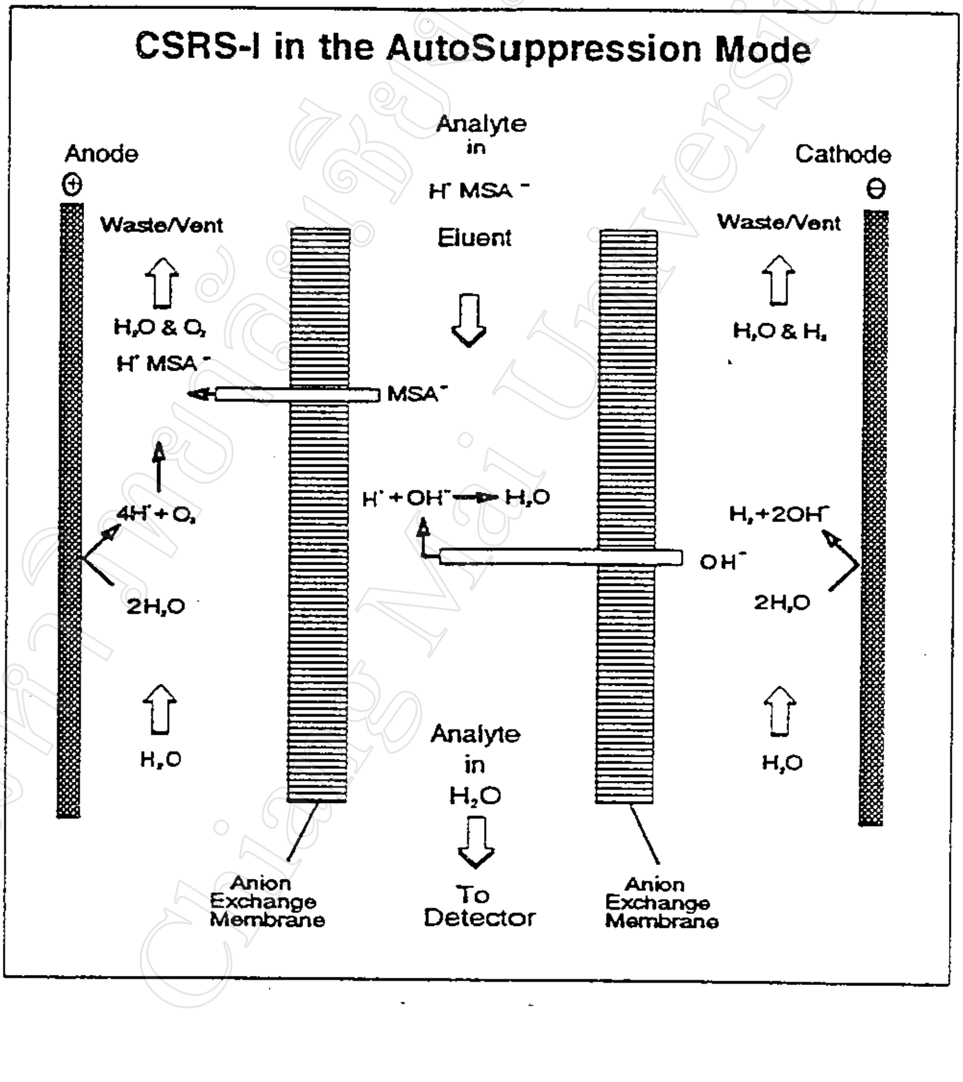

Figure 1.3 Chemical suppression with the cation self-regenerating sppressor (CSRS-1).

Chemical suppression with the cation self-regenerating suppressor is a neutralization reaction and selective desalting process carried out across the cation exchange membranes. In this mode no electrical potential is applied across the electrodes. Hydroxide ions in the chemical regenerant move across the membranes and combine with the acidic eluent cations, 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.

Detectors

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

Conductometric detection is a widely used and important part of modern IC. It is relatively a newcomer to the area of chromatographic detection while spectro-photometric detection is the most widely used detector in modern HPLC.

Conductometric detector [8]

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 electrical 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 proprotional to concentration followed by Kohlrausch's law of independent migration [9] :

$$K = \Sigma i \ \lambda i \ ci / 1000 \qquad .... (1.1)$$

K = measured concentration in S/cm

λi = ionic limiting equivalent conductivity

ci = concentration of ions in equivalent/lit

Table 1.2 Equivalent conductivities ($\lambda°$) in aqueous solution, at 25°C ($S \times cm^2/equiv$) [9].

Anions	$\lambda°$	Cations	$\lambda°$
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

Spectrophotometric detector [10]

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 sentitivity 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.

1.2.2 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 [10] :

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

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 **Figure 1.4**. Peaks are considered to be fully resolved when R = 1.5 when their separation is 99.7% complete. In most practical cases, however Rs = 1.0 corresponding to 98% separation is ususally adequate [11].

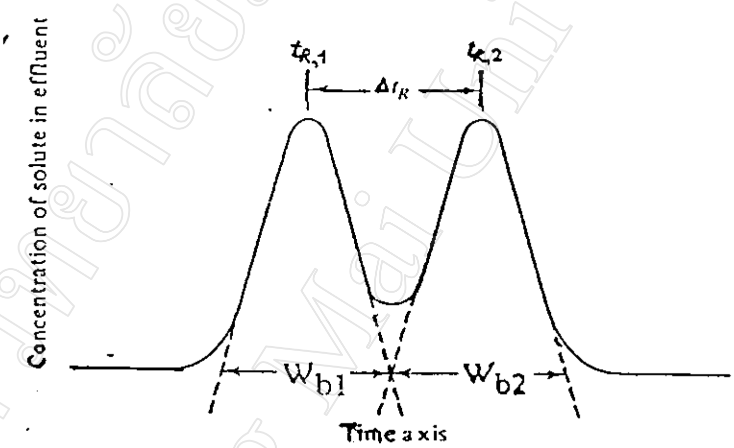

Figure 1.4 Chromatogram of two components used in the definition of resolution.

The resolution is a basic measure of efficacy 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.

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

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

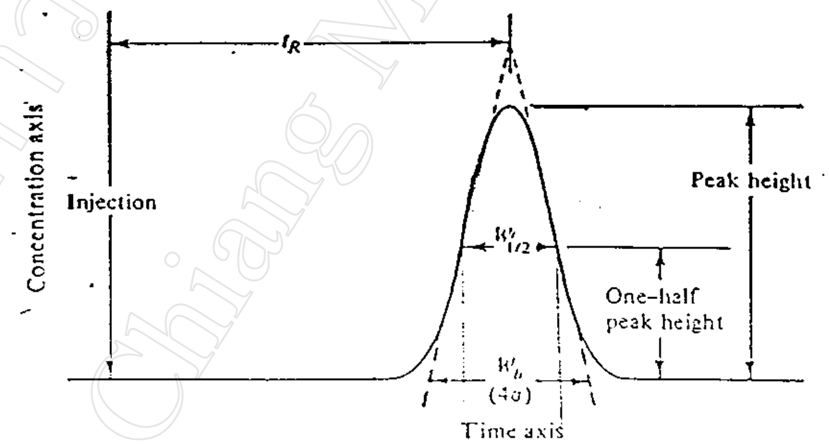

Figure 1.5 Evaluation of a chromatographic peak for column efficiency.

The height equivalent to a theoretical plate (H) as thickness of theoretical plates 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 variables 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 diffusion term

B/u = longitudinal diffusion term

Cu = mass transfer term

1.3 Anions and Cations Analysis by Ion Chromatography

Early publications of ion chromatography work described environmental applications. Since it was introduced in 1975 [3], 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 water.

Crowther and McBridge [14] employed conductometric detection to determine fluoride, chloride, nitrite, sulphate, bromide, nitrate and phosphate in rain water. Detectable concentrations of anions were in low part per billion (ppb) ranges.

Itoh and Shinbori [15] applied ion chromatography to the analysis of sea water using a 125 cm long column and a conductometric detector. This technique provided a simple and sensitive analytical method for brine samples. However, nitrite could not be determined owing to the presence of a large chloride peak.

Lee and Field [16] employed a post column cerium fluorescence detection system to determine nitrite and nitrate in drinking water and sea water. The use of a pretreatment column in the silver form for removal of chloride has been reported [3].

Fritz and his co-workers [17,18] reported the separation of alkaline earth metal ions on a low-capacity cation-exchange resin with post column derivatization and spectrophotometric detection. However, with post column derivatization the analytical precision is sometimes influenced by the pumping delivery system.

Atwood and Wallwey [19] developed to simultaneously analyze for monovalent and divalent cations. Data was compared to inductively coupled argon plasma (ICAP). The IC method gave an excellent separation and eliminated any need for matrix matching of samples and standards. Low levels of magnesium, calcium, strontium and barium may be detected in samples with high sodium and/or potassium content. Detection limits at or below 0.1 mg/L are possible in this complex matrix.

In this work, suppressed ion chromatography and post column derivatization were 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-}, Ca^{2+}, Mg^{2+}, Sr^{2+}, Pb^{2+} , Cu^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+}. Suppression mode was necessary in this work when detection was made on a conductivity detector, a universal detector capable of detecting any 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.

1.4 The Scope and Aims of This Research

The chromatographic conditions of three systems of ion chromatography, namely, an anion micromembrane suppressor, a cation micromembrane suppressor and post column derivatization, were optimized for simultaneous determinations of anions and cations. The obtained conditions were applied to determine the amounts of anions and cations in some potable drinking water and well water samples. The obtained results were quantitatively compared with data obtained from the spectrophotometric (uv-vis) [20,21] and the atomic absorption spectrophotometric (AAS) techniques [22,23].

The aims of this research are as follows.

1. To investigate and obtain optimum ion chromatographic conditions for simultaneous determination of ions of interest, including F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Sr^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+} and Ni^{2+}.

2. To apply the obtained conditions to the analysis of anions and cations in some potable drinking water and well water in the area of Muang District of Chiang Mai Province of Thailand.

3. To compare results between the ion chromatographic technique and the spectrophotometric (uv-vis) and the atomic absorption spectrophotometric (AAS) techniques.