1-1 Non suppressed ion chromatography method to separate and determinate:

1-1-1- Inorganic anions:

A number of alternative method have been reported in the literature all of which use an analytical separator column without suppressor\(^1\). So there are many application used this method for determination of inorganic anions in several extent. Ion chromatography (IC) has been applied successfully to the determination of ions in diverse type of environmental sample\(^2,3,4\). M. E. Fernande-Boy and et al\(^5\), proposed that (SCIC) is valuable technique for analysis of inorganic anions in drainage water and soil solution samples. (Cl\(^-\), NO\(_2^-\), NO\(_3^-\), HPO\(_4^{2-}\), SO\(_4^{2-}\)) can be determined simultaneously by (SCIC) using low conductivity mobile phase (270 µs/cm) 1.3 mM Sodium borate + 1.3 mM sodium gluconate containing 12% acetonitrile (ACN) (v/v) at pH (8.5) and at flow rate of 1.2 ml/min, The separation go on a low-capacity waters IC-pack A column polymethacrylate resin with quaternary ammonium functional group.

The result obtained by this method were in good agreement compared with those obtained by traditional method, because SCIC added advantage of being a rapid and sensitive method, it has minimum detection limits (0.02 – 1.25 ppm) and separation time
within 10 min. Compared to non-chromatographic techniques ion chromatography has the advantages of separation before detection increased sensitivity, simple sample preparation and faster analysis time\(^{(6,7)}\).

Compared with suppressed ion chromatography, in a single column ion chromatography (SCIC), the capacity of several column to operate without suppressor column devices simplifies equipment requirement and enhance ease of use\(^{(6,8)}\). In the mid to late 1970s, several workers experimented with changing the capacity of ion exchange resin\(^{(9)}\).

It was found that a significant reduction in resin ion exchange capacity will permit a substantial reduction in eluent ion concentration while maintaining retention times of analyte ion in a desirable range\(^{(10,11)}\).

T. balanco\(^{(12)}\) described a non-suppressor chromatographic method with conductometric detection for the simultaneous determination of (F\(^-\), Cl\(^-\), NO\(_2^-\), Br\(^-\), NO\(_3^-\), and SO\(_4^{2-}\)) in drinking water. The separation was achieved using a low capacity anion exchange column packed (Metrohm IC Anion column) with polymethacrylate with quaternary ammonium groups, and using a mobile phase consisting of 1.8 mM phthalic acid + 2 amino-2-hydromethyl-1,3 propendiol containing 8.1% aceto-nitrile (ACN) in pH (4.2) at a flow rate of 1.5 ml/min.
For achieve the desired separation and improve performance characteristic of this method, four ion chromatographic parameters were optimized, eluent flow rate, pH of eluent, concentration of phthalic acid in eluent and concentration of acetonitrile (ACN) in eluent. So this method has numerous advantages over the other widely used non-suppressed ion chromatography method: higher selectivity, shorter analysis time (8 min), lower quantitation and low detection limits (0.003 – 0.004 ppm). Also, it is characterized by high accuracy precision and linearity.

Ion chromatography finds general application in food analysis. The chemical composition of honey has been treated for a long time but nowadays this subject became even more interesting, the determination of common anions has not been described for honey, perhaps due to problems associated with great matrix influence, mainly in oxalate analysis\(^{(13)}\). In the determination of organic acid in honey usually oxalic acid does not appear\(^{(14,15)}\) probably due to its lower retention. So, a method that could be useful for oxalic determination in honey using ion-exclusion chromatography with electrospray mass spectrometry has been proposed\(^{(16)}\). Obviously a lot of options have been proposed to evaluate anions in many different matrixes, among them the most used are capillary electrophoresis and ion chromatography. M. J. del nozal\(^{(17)}\), developed the method to the quantitation of oxalate, SO\(_4^{2-}\) and NO\(_3^-\)
in honey and honeydew and gives idea of the approximate content of \( \text{H}_2\text{PO}_4^- \). To prevent matrix interference and to isolate the anions, a clean-up step using solid-phase extraction on anionic cartridges and elute with 0.01M chromate solution.

The anions are separated on an anionic column (150 × 4.6 mm I.D) IC-pack A-HC from Waters, packed with 10 \( \mu \)m particles, with a mobile phase of 1.4% lithium borate-gluconate + 2% n-butanol + 12% acetonitrile and water (84.6%) at a flow rate of 2 ml/min and using the conductimetric detection. The detection limits were calculated as a signal-to-noise ratio of 3 were found to be 0.122 ppm for \( \text{NO}_3^- \), 1.798 ppm for \( \text{SO}_4^{2-} \) and 1.547 ppm for oxalate.

Also, ion chromatographic methods are routinely used in sugar laboratories for analysis of sugar and other compounds. S. N. Walford\(^{(18)}\) used 4 mM P-hydroxybenzoic acid containing 2.5% Methanol, to separate (\( \text{Cl}^-\), \( \text{H}_2\text{PO}_4^-\), \( \text{SO}_4^{2-}\)) on the anion exchange column, the minimum detection was calculated at signal-to-noise ratio of 3 was found to be 0.1 ppm for chloride, 0.8 ppm for Phosphate and 0.2 ppm for Sulfate. Also IC is wide diffused for analysis anion in wines since it requires a minimal handling of sample and allows simultaneous analysis\(^{(19)}\), Pera et al\(^{(20)}\) can determined the concentration of inorganic anions (\( \text{Cl}^-\), \( \text{SO}_4^{2-}\), \( \text{NO}_3^-\)) in different type of marsala wines, with a conductivity detector without suppression and using A metrosep anion dual 1 column (3 × 150 mm) packed with quaternary ammonium
polymethacrylate, with a mobile phase of 8 mM phthalic acid containing 2% (ACN), PH 4.0 and tris buffer was used flowing at 0.5 ml/min. In this conditions, the detection limits of 0.17, 0.09, 0.18 ppm respectively, for Chloride, nitrate and sulfate were achieved, which are much lower than those reported by literature (21) 0.31, 0.70, 1.90 ppm respectively for Chloride, nitrate and sulfate.

S. J. Azhari (22) proposed a sensitive and simple analytical method for simultaneous separation and determination of common inorganic anions (F⁻, Cl⁻, Br⁻, NO₃⁻, I⁻ and SO₄²⁻). The separation was achieved on the anion exchange column Shimpack IC A1, (4.6 mm I.D. × 100 mm) with mobile phase consisting of 2.2 mM phthalic acid + 2.7 mM of tris- (Hydroxymethyl aminomethane) and 0.2 mM N-{[(ethylamino) thioxomethyl] hydrazinocarbonylmethyl}trimethyl ammonium chloride (ETHTC) with a flow rate of 1.5 ml/min. In this study the retention time sharply decrease when the (ETHTC) are contained in the composition of mobile phase from 16.929 to 11.880 min. So this proposed method has numerous advantages, higher sensitivity, shorter analysis time, lower quantization and detection limits ranging from 0.0022 to 0.0035 ppm. the min of this work is to improve and characterize the method for simultaneous determination of these six inorganic anions in some medicinal plants which are existing in different places at Saudi Arabia.
In non suppressed anion chromatography often gives a second system peak (SP) due to distribution of the conjugate acid of the eluting ion to the stationary phase \(^{(23-25)}\), in the previous work \(^{(26,27)}\) they proved that the detection sensitivities of the inorganic common anions eluted between the void and the 2\(^{nd}\) SP are significantly increased by using an organic strong acid such as 5-Sulfoisophtalic acid as the eluent, but when using a commercially available anion exchange column the peak of Cl\(^-\) and NO\(_2^-\) ions was overlap, in order to solve this problem another high-resolution column must be found. Y. Yokoyama, et al \(^{(28)}\) proposed the optimum combination for a high resolution and high sensitivity anions IC system using 1.5 mM 5-Sulfoisophtalic acid as eluent and low-capacity anion exchange column prepared by modifying octadecyl-silica (ODS) materials with cetyltrimethyl-ammonium salt (CTA\(^+\)), under these conditions (H\(_2\)PO\(_4^-\), Cl\(^-\), NO\(_2^-\), Br\(^-\), NO\(_3^-\) and SO\(_4^{2-}\)) can be separate and determinate, and NO\(_2^-\) was separate from Cl\(^-\) and it's peak shape was also improved, Also the 2\(^{nd}\) SP appeared at 25 min which led to a parcial cycle time of 30 min. And the 1\(^{st}\) SP is fairly small compared with those observed in conventional IC separation. So these method considered to be very practical and applicable to analysis of actual samples such as environmental water.
1-1-2 Mixture of Inorganic anions and Organic acids:

Ion-exchange chromatography is widely used for the separation of inorganic anions and organic acid which can partly be dissociated to anionic forms in aqueous solution. In recent years, several methods for the simultaneous separation of organic acid and inorganic anions were developed (29-35). Non-suppressed IC with conductivity detection, in which a low-conductivity eluent is used, is an obvious alternative for the simultaneous determination of organic acid and inorganic anions in food samples (32).

Potassium hydrogen phthalate (KHPh) eluent is used most widely in non-suppressed IC. However, a negative peak influences the determination of acetic and lactic acids for alcoholic drink (33), or ascorbic acid for tea samples. In addition, H$_2$PO$_4^-$ and succinic acid in tea can not be separated. In order to resolve these problems, M. Y. Ding (19) developed the method for the simultaneous analysis of organic acid and inorganic anions in tea samples. The separation go on the anion exchange column shim-pack IC-A1 (100 mm x 4.6 mm I.D.) with mobile phase consisting of 0.75 mM KHPh and 0.25 mM phthalic acid with pH 3.5 with a flow rate of 1.0 ml/min and using conductometric detection, the analysis time was 40 min and the detection limits were 0.58, 0.96, 1.04, 0.50, 0.58, 1.34, 0.48, 0.12, 0.044, 0.13, 0.14, 0.11 and 0.19 for (acetic acid, ascorbic acid, succinic acid, formic acid,
malic acid, citric acid, tartaric acid, H$_2$PO$_4^-$, Cl$^-$, NO$_2^-$, Br$^-$, NO$_3^-$ and SO$_4^{2-}$) respectively. In this method the inorganic anions and organic acids were separated without interference peaks, except of NO$_2^-$ and malonic acid peaks there were interference. Ion chromatography (IC) has widely recognized as a useful technique which offers advantages for the analysis of drinking water and ecological samples e.g., rain water, snow, ice core, mineral water, ground water and sea water. S. J. Azhari was sought to develop a rapid quantitative and highly sensitive analytical method for simultaneous separation and determination of seven inorganic anions and eight organic acids namely acetic acid, ascorbic acid, succinic acid, F$^-$, lactic acid, malic acid, Cl$^-$, malonic acid, NO$_2^-$, citric acid, Br$^-$, NO$_3^-$, Oxalic acid, I and SO$_4^{2-}$, by non-suppressed ion chromatography and conductivity detection. The separation was carried out using an anion exchange column (shim pack IC Al, 4.6 mm I.D × 100 mm) with the mobile phase consisting of 2.4 mM phthalic acid and 2.3 mM tris (Hydroxymethyl amino methane) with a flow rate of 1.5 ml/min. In this study the retention time achieved is short (17.267 min) for 15 species comparing with that achieved with Ding's method. In addition to this the interference of malonic acid and NO$_2^-$ which has been reported in Ding's method has been solved. So, this method has been successfully applied to 22 Saudi Arabia
commercially available bottled drinking water. Also it has detection limits ranging from 0.02 to 0.65 ppm.

Inorganic and carboxylic acids contribute to the final acidity of the coffee beverages, acidity being associated with a better flavor and aroma \(^{(48)}\). The analysis of these compounds in tea and coffee by high-performance liquid chromatography (HPLC) has been reported in the literature by several authors \(^{(49-51)}\).

Pablos and A. G. Gonzalez \(^{(52)}\) proposed the method for simultaneous determination of inorganic anions and organic acid. These are (Acetic, malic, ascorbic, citric and succinic acids, Cl\(^-\) and H\(_2\)PO\(_4\)\(^-\)) \(^{-}\). The separation is performed on an anion-exchange column (150 × 4.1 mm) using an isocratic elution with 0.6 mM aqueous potassium hydrogen phthalate (KHPh) pH (4.0) containing 4 % (v/v) acetonitrile as mobile phase at a flow rate of 1.0 ml/min and detect with conductimetric detection. In this method the authors have studied the effect of organic solvent to improve the resolution of some peaks. So they used the acetonitrile (ACN) as the organic additive to improve the overlap between malic and Cl\(^-\) peaks. Therefore this method has right selectivity because the peaks showed resolutions ≥ 1.5 for all the determined compounds, moreover the limits of detection in (ppm) were 2.0 for acetic acid, 12.6 for ascorbic acid, 6.4 for citric acid, 1.7 for malic acid, 1.5 for succinic acid, 0.6 for Cl\(^-\) and 4.1 for H\(_2\)PO\(_4\)\(^-\).
The method was successfully applied to the analysis of tea and coffee samples without interferences.

S. J. Azhari\textsuperscript{(53)}, developed a very rapid and sensitive method of non-suppressed conductivity detection ion chromatography for the simultaneous separation and determination of common inorganic anions and organic acid the separation was performed on an anion-exchange column (shim pack IC A1, 100 mm x 4.6 mm I.D) within 11.698 min, by isocratic elution with 2.2 mM phthalic acid + aqueous mixture of 2.7 mM tris (hydroxy-methyl) aminomethane + 0.2 mM of N-\{[(ethylamino)thioxo-methyl] hydrazinocarbonylmethyl\} trimethyl ammonium chloride (ETHTC) and pH 3.70 as eluent at a flow rate of 1.5 ml/min.

Four parameters are used for optimization including concentration of phthalic acid, eluent flow rate, pH of eluent and column temperature. Also this developed has been examination the effective of ligand (ETHTC) in the composition of mobile phase in order to obtain the best separation. So this study is more satisfactory comparing with the work of Pablos et al\textsuperscript{(52)} in that method they separated six acids and two ions with 25 min. But the method proposed by Azhari\textsuperscript{(53)} separated of 8 acids (acetic, ascorbic, succinic, lactic, formic, citric, tartaric and oxalic) and 6 anions (F\textsuperscript{−}, Cl\textsuperscript{−}, Br\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, I\textsuperscript{−} and SO\textsubscript{4}\textsuperscript{2−}) and the time of separation is 11.698 min. Also the LOD for this study ranged from
0.018 to 0.096 ppm for organic acids and from 0.0023 to 0.0056 ppm for inorganic anions. Moreover, this method was successfully applied for the analysis of some medicinal plants grown in kingdom of Saudi Arabia.

When analyzed organic acids and inorganic anions by non-suppressed IC, aromatic compounds are usually used as a mobile phase, they have low background conductivity and, therefore to an increase in detection sensitivity. K. Yoshikawa et al.\(^{(54)}\) established optimal condition of simultaneous determination of six organic acids (acetic, lactic, succinic, malic, tartaric and citric acids) and four inorganic anions (Cl\(^{-}\), NO\(_2\)\(^{-}\), NO\(_3\)\(^{-}\) and SO\(_4\)\(^{2-}\)) according to a non-suppressed ion chromatography coupled with conductivity detector, and the separation column was a carbon IC BI-01 (100 mm×4.6 mm I.D) coated with cetyltrimethylammonium (CTMA).

In this study two mobile phase with low conductance were checked (1) salicylic acid and sodium salicylate (2) benzioic acid and tris aminomethane. When salicylic acid and sodium salicylate used as a mobile phase each organic acid are analyzed approximately 10 min (except SO\(_4\)\(^{2-}\)) but the separation of malic acid, chloride and nitrite was difficult. When benzoic acid and 2-amino-2-hydroxy methyle-1,3-puropanediol (tris aminomethane) were used as a mobile phase, tartaric acid and citric acid, etc. With large valency showed tendency to which the width of each peaks extend and
retention time increased. However, it was possible to separate excellently for the analyte detected within 10 min (except $SO_4^{2-}$). Especially the separation of the $Cl^-$, $NO_2^-$ and malic acid became possible.

This method showed excellent linearity, reproducibility and the detection limits of organic acids were between 1.2 and 4.5 ppm. Therefore it was applied to the determination of organic acid in food samples such as nutritious, vinegar and yogurt without matrix effect.
1-2- Suppressed ion chromatography method to separate and determine:

1-2-1- Inorganic anions:

Ion chromatography has been a well established method of analysis for a number of years. It is particularly suited for the analysis of anions due to its cost and its universal detection capability\(^{(55-61)}\). Lamb et al\(^{(62)}\) described a method to separate inorganic anions, such as (F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), SO\(_4\)^{2-}, NO\(_3^-\), HPO\(_4\)^{2-} and ClO\(_4^-\)) in drinking water by using macrocycle-based ion chromatography. The separation was achieved on IonPac NS1 (4 mm) analytical column, and 5 mM KOH + 0.5 mM 18-crown-6 was used in isocratic mod with flow-rate 1.0 ml/min and the separation time was achieved in 8 min.

Zhu et al\(^{(63)}\) developed an ion chromatography method for the simultaneous determination of trace (IO\(_3^-\), ClO\(_2^-\), BrO\(_3^-\), NO\(_2^-\), Br\(^-\) and ClO\(_3^-\)) in drinking water by using IonPac AS9-HC analytical column (250 mm \(\times\) 4 mm I.D) and the suppressed conductivity detector, with the mobile phase of 8.0 mM Na\(_2\)CO\(_3\) with flow-rate of 1.3 ml/min, the method detection limits were achieved in less than 17 min.
Mou et al. (64), proposed a simple and convenient method for the preconcentration with microwave-assisted evaporation. The method allows the simultaneous separation and determination some anions such as (F\(^-\), Cl\(^-\), NO\(_2\)\(^-\), NO\(_3\)\(^-\), IO\(_3\)\(^-\), ClO\(_3\)\(^-\), BrO\(_3\)\(^-\) and ClO\(_4\)\(^-\)) in drinking water, by one injection with a high-capacity anion-exchange column IonPac AS16 (250×4 mm) with suppressed conductivity detection and NaOH eluent in linear gradient at flow-rate of 1.0 ml/min. The all anions were analyzed within 35 min with LOD between 0.10 to 0.36 ppb.

Disinfection of drinking, mineral and table water as well as of pool water is carried out to preserve public health. The chemically reactive disinfectants produce disinfection by-products (DBPs) by reacting with substances in the water. Discussion about the inorganic DBPs like bromate, chlorite and chlorat is becoming more and more popular and many papers take up this (65-67). For the first time, an ion chromatography method for the simultaneous determination of the disinfection by-products (bromate, chlorite, chlorate and seven standered anions (F\(^-\), Cl\(^-\), NO\(_2\)\(^-\), SO\(_4\)\(^2-\), Br\(^-\), NO\(_3\)\(^-\) and HPO\(_4\)\(^2-\)) is presented (68) the separation of all these anions was carried out using a laboratory-made PV/DVB anion-exchanger with 2-(dimethylamino)-ethanol as the functional group. Using mobile phase consisting of 10 mM NaOH + 0.5 mM HClO\(_4\) with flow rate 1.0 ml/min this developed
method is a sensitive tool for the analysis of the inorganic anions, so this method enables the simultaneous determination of those anions by a single injection without any sample pretreatment. The LOD for bromate measured in deionized water is 0.1 ppb and for chlorite, it is 0.7 ppb and the method's LOD for the other eight anions are between 0.1 and 1.6 ppm.

It is important to determinate trace levels of some inorganic anions as fluoride, chloride, bromide, nitrate, nitrite, sulphate or phosphate because they are naturally present in the crude matter and may also be introduced during industrial manipulations\(^{(50,69)}\). The analysis of inorganic anions in food sample is important from the nutritional toxicological and technological point of view. IC is the most effective method for anion analysis owing to its precision, high sensitivity and rapidity coupled with the advantage of simultaneous determination.

Pera et al\(^{(70)}\) describes the use of ion exchange chromatography with conductivity detection and chemical suppression for the simultaneous analysis of \(\text{F}^-\), \(\text{Cl}^-\), \(\text{Br}^-\), \(\text{NO}_2^-\), \(\text{NO}_3^-\), \(\text{PO}_4^{3-}\), \(\text{SO}_4^{2-}\) and \(\text{I}^-\) in vegetable oil samples, after extraction with hot water applying ultrasound. Anion separation was achieved with a Metrosep anion Dual 1 column (3.0 \(\times\) 150 mm) packed with quaternary ammonium polymethacrylate. The isocratic elution carried out using a solution of 3.12 mM \(\text{Na}_2\text{CO}_3\) + 3.25 mM \(\text{NaHCO}_3\) containing 2% acetone, with a flow rate of 0.5 ml/min.
Under these conditions, detection limits ranging from 8.4 to 31 ppb were achieved for all the studied anions. The separation was accomplished within 27 min.

Traditional methods used for the determination of anions in environmental samples are spectrophotometric methods\(^{(71-73)}\) or electrochemical methods\(^{(74-76)}\). Ion chromatography is becoming more and more popular for the analysis of environmental samples\(^{(4,31,77-80)}\). Hyun-Mee Park, et al\(^{(81)}\) has been investigated six inorganic anions (F\(^-\), Cl\(^-\), NO\(_2^-\), NO\(_3^-\), PO\(_4^{3-}\) and SO\(_4^{2-}\)) contamination level of environmental samples in Korea, using chemically suppressed ion chromatography with conductimetric detection. The separation go on separator column IonPac AS4A-SC (4.0 × 250 mm) with the mobile phase consisting of 1.8 mM Na\(_2\)CO\(_3\) + 1.7 mM NaHCO\(_3\) and was isocratically flowed at 2 ml/min for this method the detection limit ranged within 0.05 to 0.1 ppm.

In the manufacture of semiconductor materials, a great deal of attention is focused on minimizing sources of contamination. Yield and reliability can be significantly compromised by ionic contamination\(^{(82)}\). These are many studies about analysis of trace anions in solvents\(^{(83,84)}\).
In a previous study \(^{(85)}\) they demonstrated the use of ion chromatography to determine trace anions in isopropanol. Kaiser and Rohrer \(^{(86)}\) can determinate of trace anions in organic solvent (isopropanol, acetone and N-methylpyrrolidone) by using an IonPac AS9-HC column (250 \(\times\) 2 mm) packed with a macro porous resin analytical with 2000Å pores. The eluent used in this study is 8.0 mM \(\text{Na}_2\text{CO}_3\) + 1.5 mM \(\text{NaOH}\) with flow rate of 0.25 ml/min under these condition \(\text{Cl}^-\), \(\text{SO}_4^{2-}\), \(\text{PO}_4^{3-}\) and \(\text{NO}_3^-\) were determined to sub-ppb levels with acceptable recovery. This technique can be very useful as a quality control test in many semiconductor applications.

Monolithic stationary phases have experienced a significant growth in research interest since the introduction of the first commercially available monolithic column in 2000 \(^{(87-89)}\).

C. Lucy et al \(^{(90)}\) was explored the use of latex-coated silica monolith column for ion chromatography. Silica monoliths are coated with either functionalized latex nanoparticles or with didoecyldimethylammonium bromide (DDAB), and they separate the common inorganic anions (\(\text{F}^-\), \(\text{Cl}^-\), \(\text{NO}_2^-\), \(\text{Br}^-\), \(\text{NO}_3^-\), \(\text{HPO}_4^{2-}\), \(\text{I}^-\) and \(\text{SO}_4^{2-}\)) by the mobile phase of 5.0 mM (for DDAB column) and 7.5 mM (for latex column) of 4-hydroxybenzoic acid at pH = 7 with flow rate of 1.00 ml/min with suppress-ed conductivity detection.
There are several methods reported in literature for determination of inorganic anions, including spectrophotometry, ion selective electrode analysis, flow injection analysis, and capillary electrophoresis. These methods are not able to determine the atmospheric concentration of anions simultaneously. Ion chromatography (IC) is known as an effective analytical method with higher sensitivity and lower detection limit for simultaneous determination of anions. Talebi and Abedi investigated the capability of the suppressed conductimetric detection ion chromatography for the separation and determination of inorganic anions $F^-$, $Cl^-$, $NO_3^-$, and $SO_4^{2-}$ associated with airborne particulate matter. The separation was achieved using an analytical column Metrosep Anion Dual 1 Metrohm (150 mm × 3.0 mm I.D.) and using the eluent of 2.4 mM NaHCO$_3$ + 2.5 mM Na$_2$CO$_3$, with a flow rate of 0.75 ml/min. This method presents that the ion chromatography is a sensitive and powerful technique for simultaneous determination of inorganic anions in air pollution studies, where a large number of samples should be analyzed in a short period of time.

An ion chromatography method was developed to determine trace anion ($Cl^-$, $SO_4^{2-}$, $PO_4^{3-}$) in high nitrate matrices. An EG4O eluent generator was used to prepare high-purity and carbonate–free KOH. The anions were separated on IonPac AS15 high capacity anion exchange column and detected by suppressed
conductivity detection. Method detection limits for Cl\(^-\), SO\(_4\)\(^{2-}\) and PO\(_4\)\(^{3-}\) of 150 ppb and lower were achieved.

1-2-1-i-Method for improving Limit Of Detection :-

All instrumental method has a degree of noise associated with the measurements that limit the amount of analyte that can be detected\(^{(98)}\).

The limit of detection (LOD) is the lowest concentration level that can be determined to be statistically different from an analyte blank. There are numerous way that detection limit have been defined. A generally accepted detection limit is the concentration that gives a signal three times the stander deviation of the background signal.

So for calculate the limit of detection (LOD).

\[
LOD = 3.3 \left( \frac{s}{S} \right) \quad (1-1) 
\]

Were s is stander deviation of the response; S is the slop or sensitivity of the calibration curve at levels approaching the limit. Therefore, detection limit in ion chromatography depends on several factors\(^{(99)}\) in addition to the conductivity system used. These including the sample volume, the goodness of temperature control, and the inherent sensitivity of the conductivity detector used.
Several methods have been published to improve the limits of detection for the inorganic anions and the DBPs \(^{100-102}\). Advancement in ion chromatography suppressor has been shown to improve IC separation and detection \(^{103,104}\).

R. Bose \(^{105}\) was described the application of new suppressed to solve complex anion separation problem with CO$_3^{2-}$, HCO$_3^-$ gradient. So this new advance removes the carbonic acid from suppressor effluent when CO$_3^{2-}$, HCO$_3^-$ are used as a mobile phase before it enters the conductivity detection, so this enhances detection sensitivity, reduces the background conductivity and improved the baseline stability and LOD.

In recently study \(^{106}\) a DS-plus suppressor was used for analyzing water samples. It is backed bed suppressor that operates continuously without the need for any external regenerate or reagent. They were used an anion separator column (250 x 4 mm) with the mobile phase of 3.6 mM Na$_2$CO$_3$ to separate some of inorganic anions (F$, Cl^-$, NO$_2^-$, Br$, NO_3^-$, PO$_4^{3-}$ and SO$_4^{2-}$) and some of oxyhalides. The separation was achieved within 25 min and the LOD for inorganic anions were ranged from 0.001 to 0.007 ppm.

In IC, a suppressor system is commonly used for a sensitive detection of ions \(^{41}\). Sato et al \(^{107}\) improvement and simplification of IC system by using a new type of suppresser device, which has a suppressor resin and switching valve was developed. This new developed was applied to the analysis of anions such as (F$, Cl^-$,
NO$_2^-$, Br$^-$, NO$_3^-$, PO$_4^{3-}$ and SO$_4^{2-}$). Some of eluent composition was studied to obtain higher sensitivity and better resolution, the best result achieved with 6.0 mM Na$_2$B$_4$O$_7$ + 15 mM H$_3$BO$_3$ + 0.2 mM NaHCO$_3$, and the separation go on TSKgel super IC-Anion , 150 × 4.6 mm with conductivity detection, the LOD between 1.1 – 16.4 ppb and separation time within 12 min.

Determination of anions in water by IC cannot provide sensitivity necessary for ultra pure water analysis. Discrepancy of detection limits (10$^{-8}$ to 10$^{-7}$ %) in various works is observed (43,108,109). In these publication, the data on blank experiment using large sample volume injection were absent, and simultaneous determination of F$^-$, Cl$^-$, NO$_2^-$, Br$^-$, NO$_3^-$, HPO$_4^{2-}$ and SO$_4^{2-}$ anions in water was not considered. Due to separation of water peak and F$^-$ anion peak was not achieved. Detection limits for Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ in article (110) according to the authors, were on the 10$^{-10}$ % level.

E. Kapinus et al (111) proposed the method to investigation the possibility of simultaneous determination of (F$^-$, Cl$^-$, NO$_2^-$, Br$^-$, NO$_3^-$, HPO$_4^{2-}$ and SO$_4^{2-}$) in water at 10$^{-9}$ to 10$^{-8}$ % level by ion chromatography using "star-Ion-A300" column (100 mm × 4.60 mm). Various combination of Na$_2$CO$_3$ and NaHCO$_3$ were tested as eluent, the optimum detection limits and separation of anions were obtained using 3.6 mM NaHCO$_3$ + 3.75 mM Na$_2$CO$_3$ as eluent and
0.5 ml / min as a flow rate. So, under these conditions, the reliable determination of $F^-$ and $Cl^-$ was provided.

A number of modified IC techniques have been used to attain the low detection levels required in suppressed IC \(^{(42,112-114)}\). Because of the separation and analysis of very low levels of $CH_3SO_3^-$ is difficult in the presence of relatively high $Cl^-$ levels.

Curran and Palmer\(^{(109)}\) proposed the method to resolve that problem. So, they separate and determine the levels of $(CH_3SO_3^-, Cl^-, NO_3^- \text{ and } SO_4^{2-})$ in ice cores. In this method, they used AS14 analytical column with quaternary ammonium functional groups with gradient elution by $Na_2B_4O_7$ eluent. The separation time was achieved in 24 min.

Application of ion chromatography (IC) for the analysis of anions in highly concentrated chemicals suffers from matrix effect \(^{(115)}\). Many recently studies developed to eliminate matrix interferences to improve LOD \(^{(116-121)}\). A coupled IC system could be successfully applied\(^{(122)}\) for the trace determination of anions in concentrated Nitric acid without sample preparation. $(Cl^-, PO_4^{3-} \text{ and } SO_4^{2-})$ were determined with LOD in concentrated nitric acid (69 % w/w) between 0.1 to 5 ppm.

K. Vermeiren\(^{(123)}\) proposed the two-dimensional ion exclusion chromatography / ion chromatography (IEC-IC) approach to be the method for the determination of trace anions in concentrated hydrofluoric acid. In order to achieve lower detection limits, this
method used with electrolytically generated and purified hydroxide eluent in combination with a low noise electrochemical suppressed. Compared to carbonate eluent, the achieved gain in peak height sensitivity for $\text{Cl}^-$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{PO}_4^{3-}$. The instrumental detection limits were calculated from the background noise and sensitivities were 2, 0.2, 0.4, and 1.4 ppb HF 50% (W/W) for chloride, sulfate, nitrate and phosphate, respectively.

1-2-1-ii - Column Resolution:

The resolution $R_S$ of a column provides a quantitative measure of its ability to separate two analytes. Column resolution is defined as:

$$R_S = \frac{\Delta Z}{W_A + W_B} = \frac{2\Delta Z}{W_A + W_B} = \frac{2[(t_{R})_B - (t_{R})_A]}{W_A + W_B}$$  \hspace{1cm} (1-2)

Figure (1-1) shows the significant of this term, which consists of chromatograms for species A and B on three column having different resolution. It is evident that a resolution of 1.5 gives an essentially complete separation of two components A and B, whereas a resolution of 0.75 does not.

At a resolution of 1.0, zone A contains about 4% B and zone B contains a similar amount of A.

At a resolution of 1.5, the overlap is about 0.3%.
Groundwater is a significant source of water. Chemically suppressed ion chromatography with a Dionex, Ion Pack AS11 (4 mm) anion separator column was used for analysis of major inorganic anions (Cl⁻, SO₄²⁻, NO₃⁻) in groundwater samples. The samples were analyzed after filtration and sometimes dilution, the separation was achieved using isocratic conditions with 21 mM NaOH as eluent. This method is well-suited the routine determination of these anions in groundwater and the resolution of these anions exhibit a well-defined resolution and symmetrical peaks giving results in less than 10 min, and LOD was lower than 0.1 ppm. IC has been approved for compliance monitoring of these...
inorganic anions in drinking water since the mid-1980s, as described in US. Environmental protection Agency (EPA) method 300.0\(^{(126)}\), this method specifies the use of an IonPac AS4A anion-exchange column with a carbonate-hydrogen carbonate eluent and suppressed conductivity detection for the determination of inorganic anions in environmental waters.

Hydroxide eluent have not typically been used for the routine analysis of common inorganic anions due to the lack of an appropriate hydroxide selective column and the difficulty in preparing contaminant free hydroxide eluent. So P. Jackson et al offers new approach\(^{(127)}\), which is a modification of method 300.0, and they used an IonPac AS17 column, EG40 eluent generator and potassium hydroxide gradient to the routine separation and determination of inorganic anions such as (F\(^-\), Cl\(^-\), NO\(_2\)\(^-\), Br\(^-\), NO\(_3\)\(^-\), PO\(_4\)\(^{3-}\) and SO\(_4\)\(^{2-}\)) in environmental waters. With the separation time 8 min and LOD were 2.6 to 12.3 ppb. The AS17 column provides superior retention of fluoride from the column void volume and improved resolution from small organic acids, such as formate and acetate, compared to the AS4A column specified in method 300.0. In addition, the EG40 eluent generator eliminates the need to manually prepare eluents, increasing the level of automation and ease-of-use of the ion chromatography system.
Since ion chromatography introduction in 1975, it has become a routine analytical method for the determination of inorganic ions, especially anions present in various matrices. Zhu et al. (128) proposed simple, reliable and sensitive analytical method to determine some anions in the sample of commercial tooth paste. Nine anions (F⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, PO₄³⁻, monfluorophosphate (MFP), glycerophosphate (GP), and oxalic acid) were analyzed using a gradient elution with KOH as mobile phase, IonPac AS18 as the separation column and suppressed conductivity detection. Under these conditions, the anions were analyzed within 33.43 min and the detection limit (signal to noise ratio of 3:1) was ranging from 0.0077 to 0.0010 ppm. Also the peaks showed resolutions ≥ 1.5 for all the determined compounds.

Certified reference materials (CRMs) are commercially produced as a highly concentrated solution 100 or 1000 ppm (129). IC is normally used for analyzing low concentration samples, below 10 ppm (130-133). But the direct measurement of highly concentrated solution like (CRMs) without any dilution results in a poor resolution in ion chromatography. So only a few studies for the measurement of ion concentration above 100 ppm have been done using ion chromatography (77).

J. lee et al. (134), developed a method which is able to provide a convenient resolution in an ion chromatography upon changing the composition and flow rate of eluent, and the injection volume of
samples. The separations go on IonPac AG4A-SC / AS4A-SC separator column. So, a good result and excellent resolution value reached to 1.5 were obtained using of 2.0 mM Na$_2$CO$_3$ and 2.5 mM NaHCO$_3$ as eluent, 0.5 ml / min of flow-rate, and a 5 µL sample loop. With those condition a highly concentrated CRM solution containing seven inorganic anions (F$^-$, Cl$^-$, NO$_2^-$, Br$^-$, NO$_3^-$, PO$_4^{3-}$ and SO$_4^{2-}$) could be separated within 15 min without making any diluted solution.

Fast separation have been preformed using short (≤ 5 cm) and wide columns (up to 120 mm). The recent introduction of monolithic column offers new opportunities for high resolution analytical separations at low pressure. Lucy and Pelletier was used short silica-based monolithic columns (0.5–1 cm) coated with the surfactant didodecyldimethyl-ammonium bromide (DDAB) for fast ion-exchange separation of some inorganic anions such as (IO$_3^-$, Cl$^-$, NO$_3^-$, Br$^-$, NO$_2^-$, HPO$_4^{2-}$ and SO$_4^{2-}$) in two minutes at 2 ml / min. For this separation the researcher don't used the traditional eluent for IC (OH$^-$ and CO$_3^{2-}$/HCO$_3^-$) because such alkaline eluent can not be used with silica stationary phase, which experience dissolution of pH greater than 7.5. So the eluent which they used for this method were 6 and 9 mM 4-cyanophenol at pH 7.3 and 7.4 or 5 mM 4-hydroxybenzoic acid at pH (5.6). The detection limits are between 0.06 to 0.02 ppm.
T. Okamoto et al\textsuperscript{(146)} were described the basic studies of the elution condition for several inorganic anions as (F\textsuperscript{−}, Cl\textsuperscript{−}, NO\textsubscript{2}\textsuperscript{−}, Br\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, HPO\textsubscript{4}\textsuperscript{2−} and I\textsuperscript{−} ), in order to achieve a higher resolution for the determination of those anions in pharmaceutical compounds, a graphitized carbon BI-01 (100 x 4.6 mm I.D.) column was used, and the eluent was 1mM tetrabutylammonium hydroxide (TBA) 2 mM Na\textsubscript{2}CO\textsubscript{3} containing 5% CH\textsubscript{3}CN with flow rate of 0.8 ml/min, by using this conditions a good resolution of anions was achieved within 30 min, and the detection limits of eight anions were between 0.5 and 10 ppb.

\textbf{(1-2-1-iii-) Optimization techniques of Chromatographic method :}

\[ R_s = \frac{\sqrt{N}}{4} \left( \frac{\alpha - 1}{\alpha} \right) \left( \frac{k_B}{1 + k_B} \right) \] \hspace{1cm} (1-2)

This equation serve as guides in choosing condition that lead to desired degree of resolution $R_s$ with a minimum expenditure of time. This equation made up of three parts\textsuperscript{(147)}:
(1) Efficiency of column in terms of (N) or (H)

An obvious way to improve resolution is to increase the number of plates N in column.

\[ N = 16 \left( \frac{t_R}{W} \right)^2 \]  \hspace{1cm} (1-4)

Where is \( t_R \) is the retention time of peak and \( W \) is the width of the peak at its base.

That increase the number of plates is expensive in terms of time unless the increase is achieved by reducing column length H, and not by increasing column length L. The minimizing of plate height can achieve by:

a- reducing the particle size of packing material, the diameter of the column, and thickness of the liquid film.

b- Optimization the flow rate of the mobile phase.

So efficiency has been carried out by determining H as a function of mobile phase velocity.

\[ H = A + \frac{B}{u} + Cu \]  \hspace{1cm} (1-5)

This is Van Deemter equation, where is \( u \) is the linear velocity of mobile phase, A is eddy diffusion, B is longitudinal diffusion and C is mass transfer.
(2) **Retention factor term** "$k$":

$$k = \frac{t_R - t_M}{t_M} \quad (1-6)$$

As shown fig (1-1) $t_R$ and $t_M$ are reading obtained from a chromatogram.

The retention factor is the amount of time a solute spends in the stationary phase relative to the time it spends in the mobile phase. This term depend on the properties of both the solute and the column. When the ($k$) for a solute is much less than unity, elution accrues so rapidly that accurate determination of the retention time is difficult, when ($k$) is larger than 20 to 30, elution times become inordinately long. Ideally, separation is performed under conditions in which the retention factor for the solutes in the mixture lies in range of 1 to 5.

The retention factor can often be improved by changes in the solvent composition. The $k$ is also influenced by stationary phase film thickness.

(3) **Separation factor term** ($\alpha$):

$$\alpha = \frac{\left( \frac{t_R}{t_M} \right)_B - t_M}{\left( \frac{t_R}{t_M} \right)_A - t_M} \quad (1-7)$$
The separation factor for two analytes in a column provides a measure of how well the column will separate the two. $\alpha$ is always greater than unity. Several options are available to increase $\alpha$ at the desirable range:

- a- changing the composition of the mobile phase.
- b- changing the column temperature.
- c- changing the composition of the stationary phase.
- d- using special chemical effects.

In the last few years, numerous analytical techniques applied in the geosciences. Ion chromatography (IC) has been well established as a low-cost analytical technique for determination of inorganic anions with high sensitivity. Non-suppressed and suppressed conductivity detection is the preferential modes for measuring inorganic anions. But advances in the analysis of anions by IC have shown that optimized suppressed IC system can provide detection limits that are up to 10 times lower than non-suppressed system. So, a suppressed IC method has been used to separate and determinate inorganic anions, such as (F, Cl, NO$_3$ and SO$_4^{2-}$) in stream of geothermal power plant. The authors used a mixture of 1.8 mM Na$_2$CO$_3$ and 1.7 mM NaHCO$_3$ at pH 9.39 with a flow rate of 1.5 ml/min and electrical
conductivity detector with anion-exchange column (IonPac AS4A-SC) and isocratic pump system.

The separation time was 5 min with LOD less than 0.184 ppm.

H. Nagashima and T. Okamoto\(^{(153)}\) have investigated the simultaneous determination of inorganic anions by ion chromatography using a dynamically coated graphitized carbon column with cetyltrimethylammonium (CTA) ions with suppressed conductivity detection and using 2.0 mM Na\(_2\)CO\(_3\) 1.0 mM NaHCO\(_3\) as eluent with a flow rate of 1.0 ml / min. Under these condition they can separate seven inorganic anions (F\(^-\), Cl\(^-\), NO\(_2^-\), Br\(^-\), NO\(_3^-\), HPO\(_4^{2-}\) and SO\(_4^{2-}\)) and good resolution of anions was achieved within 18 min, the LOD were between 0.2 – 3 ppb. In this method they also studied the effect of acetonitrile (ACN) added to the eluent on the analysis of common anions, so the addition of (ACN) was effective to retain F\(^-\) well out of the water dip and to isocratically separate common anions at the ppb level. So this method showed excellent reproducibility, lower detection limits and fewer interferences. A simple, rapid and accurate method\(^{(154)}\) for the determination of anionic minerals in tea brew has been developed. The quantitative determination of anions F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), NO\(_3^-\), HPO\(_4^{2-}\), and SO\(_4^{2-}\) was accomplished by anion exchange chromatography with the suppressed conductimetric detection. A Metrosep Anion Dual 2 analytical column was used for anion separation. A solution containing a mixture of 1.3 mM
Na$_2$CO$_3$ and 2 mM NaHCO$_3$ was used as eluent. The method requires a simple sample clean-up procedure to remove the interfering organic components from the tea brew. The limit of detection for different anionic minerals were in the range from 0.01 to 0.05 ppm. The method was applied to the determination of anions in black and kombucha tea.

1-2-2- Mixture of Inorganic anions and Organic acids:

Direct analysis of organic acids in the presence of common inorganic anions remains an analytical challenge$^{(155)}$. In recently study$^{(156)}$ simultaneous separation of 19 organic acids and 10 inorganic anions has been demonstrated using ion chromatography with a high capacity anion exchange column (IonPac AS11-HC, 250 mm × 4 mm) and the suppressed conductivity detection, the separation was achieved using gradient elution by several eluent composition containing 100 mM NaOH, Methanol and 1 mM NaOH.

The carboxylic acids and inorganic anions including (F$^-$, Cl$^-$, Br$^-$, I$^-$, SCN$^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$, S$_2$O$_3^{2-}$, PO$_4^{3-}$, lactate, acetate, propionate, formate, butyrate, pyruvate, glutarate, succinate, malate, tartrate, citraconate, maleate, 2-ketoglutarate,
fumarate, oxalate, citrate, isocitrate, cis-aconitate and trans-aconitate) with the analysis time about 66.8 min.

Many papers have been published on acids determination in beverages with various analytical methods such as enzymatic and (HPLC) method. But the speed and selectivity of HPLC methods render them the more useful for the analysis of juices\textsuperscript{(21,157-162)}. IC was certainly the technique of choice to separate and quantity organic acids and inorganic anions in grape juices. P. Masson\textsuperscript{(163)}, has investigated to develop a sufficiently good separation of both major and minor organic acids and inorganic anions such as (Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, succinic acid, malic acid, tartaric acid, ketoglutaric acid, fumaric acid, SO\textsubscript{4}\textsuperscript{2−}, oxalic acid, PO\textsubscript{4}\textsuperscript{3−} and citric acid) present in grape musts. In this study he used a Dionex AS11 column and NaOH gradient elution and suppressed conductivity detection. Also the influence of three different solvents (methanol, ethanol and acetonitrile) on the efficiency of column was compared. The best separation was achieved with an eluent containing NaOH gradient in water, 13% (v/v) methanol, 13% (v/v) ethanol in water. This proposed method showed high sensitivity with the separation time 20 min.

The reliable and accurate determination of anions in power plant water samples at sub-to low ppb levels is a challenging analytical problem. Over the past 20 years, ion chromatography (IC) has become an indispensable technique for addressing this problem.
because IC offers the unique capability to separate and identify individual ionic species at sub-to low ppb levels\textsuperscript{(164-170)}. So there have been several advances in IC method to improve the determination of anions at trace level.

One of these advantages was the development of new and improved electrolytic suppressor\textsuperscript{(171-172)}. These new electrolytic suppressors improve the determination of anions at trace levels because they offer several advantages such as ease of use, low baseline noise, and fast equilibration. Z. Y. Liu et al\textsuperscript{(173)} report a new IC method that utilizes that recent advantages in IC for the determination of target inorganic and organic acid anions including (F\textsuperscript{−}, acetate, formate, Cl\textsuperscript{−}, NO\textsubscript{2}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, Br\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−} and PO\textsubscript{4}\textsuperscript{3−}). Sub-to low ppb levels in power plant water samples. In this method samples were injected using a large-volume direct injection technique, the analyte anions were separated on a hydroxide-selective anion-exchange column IonPac AS15-5 µm (150 mm × 3mm I.D.). Using high-purity hydroxide eluent generated by an on-line electrolytic eluent generator and detected using the suppressed conductivity detection method. The method detection limits for analyte ions in deionized water were range from 0.079 to 0.0056 ppb.

In considering methodologies for a universal method for anions typically found in pharmaceuticals there are some chromatographic methods with suppressed\textsuperscript{(174-176)} for analysis.
A universal method (177) or quantization of anionic substances in active pharmaceutical ingredients (API) was development using (IC). A Dionex IC system was used in this study by IonPac AS11HC (250 mm × 4 mm) column and suppressed conductivity detection and gradient elution with KOH. The mobile phase including acetonitrile so under these conditions some inorganic anions and organic acid such as (F⁻, acetate, propionate, formate, Cl⁻, NO₂⁻, trifluoroacetate, Br⁻, NO₃⁻, CO₃²⁻, malate, SO₄²⁻ and PO₄³⁻) can be separate and determinate in less than 38 min.

Citrate is widely used in pharmaceutical preparation. IC with suppressed conductivity detection has been demonstrated to be a method of choice for the determination of anions, including citrate (178). De Borba et al (179) describes the development and validation of a simple, rapid, accurate and sensitive ion chromatographic procedure to assay total citrate and phosphate in pharmaceutical dosage forms. Citrate and phosphate were separated in less than 10 min by a hydroxide selective column an IonPac AS11(4 mm × 250 mm) with a 20 Mm KOH eluent and detected by suppressed conductivity. This method showed LOD for phosphate and citrate was 0.06 ppm.

Udisti et al (180), analyzed the carboxylic acids in a shallow core, using DX-4000i with AS11 as the separator column and ASRS-I as the suppressor. So they resolved with Na₂B₄O₇ eluent as low as 0.9
mM. F\(^-\), lactate, acetate and formate that are very close in affinity. Their method, however, did not separate oxalate and inorganic species. X. Lee et al\(^{(181)}\), developed a method with DX-300 ion chromatography by using AS4A-SC as separator column and ASRS-II as the suppressor and using gradient elution with Na\(_2\)B\(_4\)O\(_7\) solution. This method resolves all carboxylic acids plus inorganic anions in snow and ice F\(^-\), acetate, formate, pyruvate, methanesulfonate (MSA), Cl\(^-\), NO\(_2\)\(^-\), Br\(^-\), NO\(_3\)\(^-\), PO\(_4\)\(^{3-}\), SO\(_4\)\(^{2-}\) and oxalate. The resolution of these anions was appear in a single run of 14 min.

Hulteen and Schaible\(^{(182)}\) presented the information and discussed a method for extraction methodology for transfer of anion from the hydrofluoroether to water. Then an analytical method utilizing ion chromatography that is capable of detection of 10 anions (F\(^-\), acetate, formate, Cl\(^-\), NO\(_2\)\(^-\), Br\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^{2-}\), oxalate and PO\(_4\)\(^{3-}\)) in the ppb level have been demonstrated. The separation of anions was achieved using an IonPac (250 mm × 4 mm) analytical column and suppressor conductivity detection, by KOH gradient elution and the separation time was about 20 min.

Mostly the unsubstituted dicarboxylic acids have been addressed by determination based on gas chromatographic and ion chromatographic methods\(^{(183)}\). An ion chromatographic method was developed\(^{(184)}\) which is able to separate unsubstituted C\(_4\) dicarboxylic acids (succinic, malic, tartaric, maleic and fumaric).
besides the other unsubstituted C₂-C₅ dicarboxylic acids (oxalic, malonic and glutaric acids) as well as inorganic anions (Cl⁻, NO₃⁻, SO₄²⁻) in sample extracted from atmospheric particulate matter. For this analysis they used a Dionex AS11-HC (250 × 4.6 mm I.D) separator column, anion suppression system and conductivity detector. Several eluent composition containing NaOH and Methanol were tested in eluent gradient programs with a flow rate of 2 ml/min. the separation was complete within 30 min for all species.

The separation of major inorganic and low-molecular-mass organic anions under isocratic conditions was not possible in a single run(114,185,186). Difficulties lie mostly in the problem with separating the critical pairs of ions, such as the F⁻ and acetate, and also the acetate and formate, because they are very close in their affinities and retention times for NO₃⁻ and SO₄²⁻ become extensively long and impractical, moreover, the tailing of chromatographic signals has been observed. In order to resolve these problems, it was necessary to employ two separate runs, one by one, with a rinsing step on the same column (114,185); or to use an automatic column switching for the simultaneous separation of inorganic and organic ions on two different analytical columns (187); or to use a combination of isocratic and gradient methods (31). On the other hand, the separation of inorganic and organic anions in a single run was possible under a gradient elution (127,181,186,188,189). However, it
should be stressed that gradient elution is nowadays, on a lot of widely used types of ion chromatographs, almost impossible to apply. Also for routine analysis, isocratic elution is the preferred separation mode. In previous works \(^{190,191}\) optimal conditions were found for the separation of acetate and formate under isocratic elution on three aforementioned columns. Krata et al\(^{192}\) proposed the method to separation two organic acids (acetate and formate) and some inorganic anions (F\(^-\), Cl\(^-\), NO\(_2^-\), Br\(^-\), NO\(_3^-\), HPO\(_4^{2-}\) and SO\(_4^{2-}\)) in one analytical IC cycle under isocratic elution using suppressed conductivity detection on three different analytical columns: IonPac AS14, Allsep A-2, and IC SI-50 4E. On the IonPac AS14 column, it was impossible to separate all concerned ions in a single run. Therefore, it was necessary to apply two-step elution with different solutions as an eluent. In the case of the Allsep A-2 column, it was also impossible to separate all investigated ions in one run. The resolution of F\(^-\) and acetate was not acceptable, and it was difficult to quantify these analytes. The chromatographic signals of HPO\(_4^{2-}\) and SO\(_4^{2-}\) were broadened. Also, the results of the validation procedure were not satisfactory. Using isocratic elution and a mixture of 1.0 mM NaHCO\(_3\) plus 3.2 mM Na\(_2\)CO\(_3\) as an eluent, it was possible to resolve all concerned ions on the IC SI-50 4E column within a single run of fairly short analysis time less than 17 min. and the best LODs (0.02, 0.2, 0.16, 0.11, 0.06, 0.05, 0.04, 0.14 and 0.09 ppm for F\(^-\), acetate, formate, Cl\(^-\), NO\(_2^-\),
Br⁻, NO₃⁻, HPO₄²⁻ and SO₄²⁻, respectively) were achieved. So this column was applied for the separation of concerned ions in environmental precipitation samples such as snow, hail and rainwater.