4. Discussion and Conclusions

4.1 Discussion

In this research, the suppressed ion chromatography of anions and cations was employed with a conductivity detector whilst the post column derivatization system was used with a uv-vis detector.

In the suppressed ion chromatography of anions in this work, the column used was an IonPac AS 4 A column of 4 x 250 mm dimension. IonPac AS 4 A analytical column is composed of 16 micron polystyrene/divinylbenzene substrate agglomerated with anion exchange latex that has been completely aminated. The 0.5% crosslinked latex particles have a diameter of approximately 0.175 μm and carry the ion exchange sites. The ion exchange capacity of this column is 20 meq/column and stable between pH 0 and 14. The latex particles are strongly held to the substrate surface by electrostatic and van der Waals interactions [6]. The column used with a Dionex Anion Self-Regenerating Suppressor-(ASRS-I) requires a constant water feed through the regenerant chambers to achieve suppression. Water can be delivered to the suppressor regenerant chamber from recycled eluent in the Autosuppression Recycle Mode of operation equipped with conductivity detector [28]. The eluent system used was sodiumcarbonate/sodiumbicarbonate. The carbonate/bicarbonate mixture allows the strength of the eluent, and thus the selectivity of the system, to be changed by varying the CO_3^{2-} /HCO_3^- ratio.The suppressor reaction product is carbonic acid, H_2CO_3, which results in a low background conductivity (15-17 μS).

Firstly, elution behaviour of anions of interest, i.e., F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} and SO_4^{2-} was studied using 1.80 mM Na_2CO_3 /1.70 mM $NaHCO_3$ at the flow rate 2 ml/min as eluent. These anions were chosen by a criterion that they were likely to be contaminants in drinking water samples. From **Table 3.1** which shows the retention times of the investigated ions, it was found that the elution sequence was F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^3 and SO_4^{2-} . The order of separation can be simply explained via the affinity of the resin for various ions. In general, the affinity of an ion exchanger for an ion increases with the charge on the ion and with increasing atomic weight of the ion [29]. Thus, the affinities of the investigated ions are in the sequence : F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} and SO_4^{2-} .

Parameters affecting the sensitivity and resolution of analysis, e.g., eluent concentrations and eluent flow rates were investigated. Effects of eluent concentration on retention time, peak area and resolution are shown in **Table 3.2** (a), (b) and (c). It was found that the retention times of all ions decreased with increasing $Na_2CO_3/NaHCO_3$ concentration as eluent. Peak area of monovalent ions also tended to decrease with increasing $Na_2CO_3/NaHCO_3$ concentration while those of divalent and trivalent ions tended to increase with increasing $Na_2CO_3/NaHCO_3$ concentration, as shown in **Table 3.2** (b). **Table 3.2** (c) shows that separation efficiency decreases with increasing $Na_2CO_3/NaHCO_3$ concentration. It should be noted that the resolution for each anion pair of the same charge is not much changed whereas the resolution for each anion pair of unlike charge is changed downwards with

increasing $Na_2CO_3/NaHCO_3$ concentration, especially that for the anion pair of NO_3^- and PO_4^{3-} . The optimum $Na_2CO_3/NaHCO_3$ concentration was considered to be 1.80 mM Na_2CO_3/1.70 mM $NaHCO_3$ with the analysis time less than 7 minutes. Peak areas of anions were sufficiently high and the resolution for each anion pair was clearly abundant as the resolution value was greater than 1.5 for every pair of peaks.

The effects of the eluent flow rate on retention time, peak area, the number of theoretical plates and resolution are presented in **Table 3.3** (a), (b), (c) and (d). It was found that all retention times, peak areas, the number of theoretical plates and resolutions decreased with increasing eluent flow rate. The best result in terms of total analysis time, sensitivity, column efficiency separation factor was obtained at the eluent flow rate of 2.0 ml/min. Optimized IC conditions giving high sensitivity and good resolution of analysis are summarized in **Table 3.4.**

The linearity range for each anion was determined in the range 0.2-400 ng/μl. The results are presented in **Table 3.5**, with the linearity curve shown in **Figure 3.1** and chromatogram shown in **Figure 3.2**. The linearity range of anions covered straight lines with slope values and correlation coefficients listed in **Table 4.1.**

Table 4.1 Analytical characteristics of anions obtained with IonPac AS 4 A column under established conditions.

Ion	Linearity range (ng/μl)	Correlation Coefficient	Sensitivity (peak area x10^5)/(ng/μl)
F^-	0.2 - 200	0.9987	672
Cl^-	0.2 - 400	0.9998	1180
NO_2^-	0.2 - 200	0.9997	292
Br^-	0.2 - 100	0.9985	122
NO_3^-	0.2 - 100	0.9986	142
PO_4^{3-}	0.2 - 100	0.9984	72
SO_4^{2-}	0.2 - 100	0.9985	194

All of the linearity ranges of anions given in **Table 4.1** are seen to cover wide concentration ranges ; the range 0.2 - 100 ng/μl appears to be the most appropriate range for all the anions studied. The only manifest exception is the range for Cl^- in the range 0.2 - 400 ng/μl . The IC is suitable for analysis of high chloride samples, e.g., brine sample as long as the Cl^- ion concentration is less than about 5000 mg/L (0.5 %) [30].

The results of the investigation on the detection limit and minimum detectable quantity were determined by injection of the chosen test solution onto the IonPac AS 4 A column to produce a chromatogram with a peak height at least twice the noise level. The obtained chromatogram is shown in **Figure 3.3**.

The detection limit and minimum detectable quantity were calculated via Equations 2.1 and 2.2, as described under Section 2.3.4. The calculated results presented in **Table 3.6** indicate that the detection limits of F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} under the investigated conditions were 0.26, 0.17, 0.57, 0.58, 0.88, 0.75 and 0.20 ng, respectively , whereas the minimum detectable quantities were 0.75, 0.49, 1.74, 2.44, 3.91, 4.05 and 1.54 ng.sec, respectively.

The reproducibilities of the peak area and retention time were calculated by performing five replicate injections. The results are give in **Table 3.7** (a) and (b). The results were found to be satisfactory with the % R.S.D. value for the retention times of anions between 0.14-0.86 and that for the peak areas between 0.76-4.73.

The obtained conditions were applied to the determination of anions in the drinking water samples. Anions found in both types of drinking water samples were F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2}. Neither NO_2^- nor Br^- were found.

For quantitative purposes, the calibration curve of each anion was constructed by plotting the peak area against the concentration injected. The calibration data are presented in **Tables 3.8-3.12**. The calibration curves with correlation coefficient, r = 0.998655 to 0.999822, are presented in **Figures 3.4-3.8.** The results of the application of the method to the analysis of anions in drinking water samples are summerized in **Tables 3.13 and 3.14** and chromatograms of some drinking water samples are shown in **Figures 3.9 and 3.10.**

The results from the analysis of the samples were obtained from replicate analyses by the spike method in terms of % recovery. The results of % recovery of anions found in drinking water samples are shown in **Tables 3.15-3.19**. The values of % recovery of anions are as follows : 98.42 for F^-, 96.90 for Cl^-, 97.94 for NO_3^-, 98.17 for PO_4^{3-} and 97.42 for SO_4^{2-}. Confirmation of peaks of anions of interest in drinking water samples was made by comparison of chromatograms of water samples with those water samples spiked with each anion. It was found that peaks obtained from water samples spiked with anions were taller than that those from the unspiked samples, as shown in **Figures 3.11-3.13**. It can be seen that all results confirm that the peaks in drinking water samples were F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}, respectively.

In order to verify quantitative accuracy, the amounts of F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2} were also determined by the spectroanalytical method. In order to decide whether there was a significant difference between the results obtained by the IC technique and the spectroanalytical techniques, the t-test was conducted for the comparison. A t-test for a situation where two similar treatments on a sample need to be compared can be accomplished if the treatments are accomplished on the same sample. This statistical test is primarily used for situations such as analysis of the same sample by two methods.

The tabulated t value (t_{table}) for six degrees of freedom at 95% confidence level is 2.571. Tables 3.20-3.24 illustrate the results of comparison of F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2} obtained by the two techniques. For F^-, Cl^-, NO_3^-,

PO_4^{3-} and SO_4^{2}, it was found that the calculated t values were higher than the tabulated values. So there were significant differences in the results of F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2} analysis by the two techniques due to the fact that the IC technique possesses higher sensitivity than the spectroanalytical technique.

The second system employed in this work was suppressed ion chromatography of cations with conductivity detector. IonPac CS 12 column of 4 x 250 mm was used in the system. Its stationary phase consisted of 8.0 μm poly(ethylvinylbenzene/divinylbenzene) macroporous substrate resin possessing the carboxylic acid functionality with a capacity of 2.8 meq/column and high hydrophobicity. The column could be run with a Dionex Cation Self-Regenerating Suppressor-I (CSRS-I). It could also be used in the chemical suppression mode. In this work tetrabutylammonium hydroxide (TBAOH) was used as a chemical regenerant instead of using an applied current and deionized water. The eluent used was methansulfonic acid (MSA). This is kept in the tetrabutylammonium cation form (TBA^+) by continuously circulating TBA^+MSA^- solution over the outside of the membrane. The MSA of the eluent was thereby converted to TBA^+MSA^- which has a significantly lower conductance [26, 31].

The elution behaviour of the alkaline earth metal ions of interest, i.e., Mg^{2+}, Ca^{2+} and Sr^{2+} was studied using 20 mM MSA at the flow rate 1.0ml/min as eluent and 25 mM TBAOH at flow rate 6.0 ml/min as regenerant. These ions

were chosen by the criterion that they usually crop up in the analysis of surface water, underground water, brine, etc. and that they were likely to be contaminants. **Table 3.25** shows the retention times of the investigated ions. The following regular retention time sequence was observed : $Mg^{2+} < Ca^{2+} < Sr^{2+}$. This phenomenon can be explained via the type of counter ion which also influences the retention of solutes as it influences the exchange equilibrium constant. The exchange equilibrium constant reflects the ratio of the affinity of solute and counter ion for the ion-exchanger. In general, the ion exchanger shows the largest affinity for ions with a larger charge, smaller hydrated volume and ion with a larger polarizability [32]. Cations used as counter ion can be arranged in increasing elution strength for ion exchangers in this order : $Mg^{2+} < Ca^{2+} < Sr^{2+}$.

The parameters affecting the sensitivity and resolution of analysis, such as eluent concentrations and eluent flow rates, were investigated and the results are given in **Table 3.26** (a), (b) and (c) which show effects of eluent concentration on retention time, peak area and resolution, respectively. It can be seen that the retention times of all ions decreased with increasing MSA concentration. Peak area of divalent ions tended to decrease with increasing MSA concentration, as shown in **Table 3.26** (b). **Table 3.26** (c) shows a decrease in separation efficiency with increasing MSA concentration. The optimum MSA concentration was considered to be 20 mM with the analysis time of 12 minutes for three ions. Peak areas of ions were adequately high and the resolution for each metal ion pair was greater than 1.5 for every pair of peaks, indicating that their separation was complete.

The effects of the eluent flow rate on the retention time, peak area, the number of theoretical plates and resolution are shown in **Tables 3.27** (a), (b), (c) and (d). It was found that retention time, peak areas, the number of theoretical plates and resolution decreased with increasing eluent flow rate. The best eluent flow rate was found to be at 1.0 ml/min because it yielded reasonable total analysis time and high sensitivity, column efficiency and separation factor.

Optimized IC conditions yielding high sensitivity and good resolution of analysis are summerized in **Table 3.28**.

The linearity ranges for ions were determined in the range 0.2-300.0 ng/μl. The results are presented in **Table 3.29**. The linearity curves are shown in **Figure 3.14** and the chromatogram of these ions is shown in **Figure 3.15**. The linearity range of cations covered the straight line with slope values and correlation coefficients, as listed in **Table 4.2**.

Table 4.2 Analytical characterestics of cations obtained with IonPac CS 12 column under established conditions.

Ion	Linearity range (ng/μl)	Correlation Coefficient	Sensitivity (peak area x10^5)/(ng/μl)
Mg^{2+}	0.2 - 100.0	0.9976	327
Ca^{2+}	0.2 - 200.0	0.9983	375
Sr^{2+}	0.2 - 100.0	0.9936	83

The method shows good linearity for all of the studied ions, with $r > 0.99$ up to 100.0 ng/μl for Mg^{2+} and Sr^{2+} while the linear range for Ca^{2+} occupied the 0.2-200.0 ng/μl concentration range. A primary requirement of a detector is that it should be responsive over a wide range of concentrations of the monitored solute. The magnitude of change of signal per unit change in concentration of analyte is often called the response of the detector. The signal induced per unit amount of analyte is often refered to as the sensitivity of the detector. Therefore sensitivity of the detector for ions was found to have decreased in the order : $Sr^{2+} > Mg^{2+} \sim Ca^{2+}$.

The detection limit and minimum detectable quantity were determined by injecting the lowest concentration of the ion mixture, giving a peak height at least twice the noise level, onto the column to produce a chromatogram. The obtained chromatogram is shown in **Figure 3.16**. The detection limit and minimum detectable quantity were calculated via Equations 2.1 and 2.2 as described under Section 2.3.4. The calculated results presented in **Table 3.30** indicate that the detection limits of Mg^{2+} , Ca^{2+} and Sr^{2+} under the investigated condition were 0.18, 0.08 and 4.75 ng, respectively, whereas the mininum detectable quantities were 1.73, 0.96 and 53.01 ng.sec, respectively.

The reproducibilities of the paek area and retention time were calculated by performing five replicate injections. Precision may be defined as the concordance of a series of measurements of the same quantity. The results are given in **Table 3.31** (a) and (b). It can be seen that the relative standard deviations (% RSD) of the retention times of the cations are between 0.072-0.340 and those of peak areas are between 0.460-3.656. These small values of the relative standard deviation indicate that the precision of analysis is high.

The obtained conditions were applied to the determination of alkaline earth metals in drinking water samples. Both types of drinking water samples were found to contain Mg^{2+} , Ca^{2+} and Sr^{2+} . Quantitative analyses of these cations were processed by the external standard method. The calibration curve of each cation was constructed by plotting the peak area against concentration injected. The calibration data are presented in **Tables 3.32-3.34**. The calibration curves with correlation coefficient, r = 0.991492 to 0.999398, are shown in **Figures 3.17-3.19**. The results of analysis are summarized and presented in **Table 3.35**. It was found that the concentrations of cations lie between the following ranges : 0.02-15.12 ng/μl for Mg^{2+} , 0.10-68.77 ng/μl for Ca^{2+} and 0.17-0.21 ng/μl of Sr^{2+} . Chromatograms of some drinking water samples are shown in **Figures 3.20 and 3.21**.

To confirm peaks of interest in drinking water samples, they were simply identified by means of retention time coincidence. Spiking method was used to determine the % recovery. The results of % recovery found in drinking water samples are shown in **Tables 3.36-3.38**. The values of % recovery of cations are the following : 96.69 for Mg^{2+} , 97.14 for Ca^{2+} and 95.48 for Sr^{2+} . Chromatograms of w.w.$_1$ sample and w.w.$_1$ sample spiked with standard Mg^{2+} , Ca^{2+} and Sr^{2+} solution at various concentrations are compared in **Figure 3.22**.

For the purpose of quantitative accuracy verification, the amounts of Mg^{2+} , Ca^{2+} and Sr^{2+} were also determined by the AAS technique. In order to decide whether there was a significant difference between the results obtained by the IC technique and the AAS technique, the t-test with multiple samples [25] was conducted for the comparison.

The tabulated t value (t_{table}) for six degrees of freedom at 95% confidence level is 2.571. **Tables 3.39 and 3.40** illustrate the results of comparison of amounts of Mg^{2+} and Ca^{2+} obtained by the two techniques. For both Mg^{2+} and Ca^{2+} , the accuracy of analysis between the two techniques was the same since $t_{calc.}$ value is smaller than t_{table}.

In the post-column derivatization system in this work, the column used was an IonPac CS 5 column, with the following characteristics : 13 μm of particle diameter, 2% substrate cross-linking, 110 nm of latex diameter, 2% latex cross-linking, 150 μeq of sulfonic acid, 70 μeq alkanol quanternary ammonium functionalities and low hydrophobicity. The most common factors of on-line chromatographic detection of transition metals is post-column derivatization using a metallochromic indicator with subsequent absorbance detection. The non-specific metallochromic indicator 4-(2-pyridylazo) resorcinol (PAR) was used in this research. The PAR-metal complexes show relatively high molar absorptivities (> 20000) in the 500-540 nm range while the reagent itself shows relatively low background absorbance at the monitoring wavelengths [33-34]. The post-column reagent in the operation of this system was forced to diffuse under helium gas pressure into the column effuent

through a permeable fiber membrane to yield complexes which could be detected by a uv/vis detector. Metal ions of interest chosen were Pb^{2+} , Cu^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+} as they were likely to be contaminants in drinking water samples. Since the post-column derivaltization detection system was used, it was necessary to find a suitable colour-forming reagent for complexation with the studied metals. **Tables 3.41 and 3.42** list the absorbance values for colour-forming reagent of metal-PAR complexes under different conditions and the resultant complexes with relatively high absorbance (λ max). The metal-PAR complexes in the presence of oxalic acid pH 5.3 as buffer was found to give higher absorbance than complexes in the presence of deionized water. The elution behavior of the metal ions were studied using 50 mM oxalic pH 5.3 at the flow rate 1.0 ml/min as eluent and 4.0×10^{-4} M 3.0 M NH_4OH/1.0 M CH_3COOH at the flow rate 0.5 ml/min as the post-column reagent and λ max at 510 nM. **Table 3.43** shows the retention times of the investigated ions. It was found that the elution sequence was Pb^{2+} , Cu^{2+} ,Mn^{2+}, Zn^{2+} and Ni^{2+} , with the analysis time of 14 minutes for five ions.

The factors which affect the separation efficiency and sensitivity were studied to obtain optimized analysis conditions. These factors are listed as follows :

- o Effects of eluent pH
- o Optimum detection wavelength
- o Effect of eluent flow rate
- o Effect of eluent concentration

Effect of Eluent pH

Post column reagent conditions were selected such that the resultant pH of the combined column eluent oxalic acid solution was greater than pH 5.0. A decrease in the eluent pH increases the retention time of the analytes [35].

Table 3.44 shows the effect of eluent pH on resolution of each metal ion pair at various eluent pH values between 3.8-6.3. It was found that eluent pH at 5.3 yielded the shortest analysis time and the resolution for any of the metal ion pairs was greater than 1.5, indicating that separation between the components was adequate [10] and there would be no need to use other eluent pH values with higher resolution. Effects of the eluent pH on retention times of Pb^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+} and Ni^{2+} are shown in **Figure 3.23**.

Optimum detection wavelength

Spectrophotometers are responsive only to those materials that absorb in the uv or visibel range of the spectrum. Therefore, the wavelength of the uv/vis detector used could affect the peak area of each metal ion. Peak areas of the metal ions were plotted against the wavelengths, as shown in **Figure 3.24**. It could be seen from this figure that the optimum detection wavelength was 510 nm.

Effect of eluent flow rate

The resolution, peak area and the number of theoretical plates were found to depend on the eluent flow rate. **Table 3.45** shows that the resolution of each metal ion pair at various eluent flow rates decreased when the eluent flow rate was increased. **Figure 3.25** shows the peak area of each metal ion against the eluent flow rate which indicated that each metal ion peak area

decreased regularly with increasing eluent flow rate. The number of theoretical plates also tended to decrease when the eluent flow rate was increased, as shown in **Table 3.46**. In order to obtain high sensitivity and high column efficiency with reasonable analysis time, the eluent flow rate at 1.0 ml/min was chosen.

Effects of eluent concentration

The optimum eluent concentration was found to be 50 mM. The dependence of the retention times, peak area and resolution on the concentration of eluent could be seen in **Table 3.47** (a), (b) and (c). It was found that when 50 mM oxalic acid pH 5.3 was used as eluent, the highest analysis sensitivity was obtained and resolution of each metal ion pair was well separated within an acceptable value > 1.5.

The optimum conditions obtained with the IonPac CS 5 column for the analysis of metal ions in this work are summarized in **Table 3.48**.

The linearity ranges for the metal ions were examined and the results are shown in **Table 3.49** and the linearity curve is shown in **Figure 3.26**. The chromatogram of Pb^{2+} , Cu^{2+} ,Mn^{2+}, Zn^{2+} and Ni^{2+} obtained with IonPac CS 5 column is shown in **Figure 3.27**. Analytical characteristics of the metal ions studied which are based on the data derived from **Figure 3.26** are presented in **Table 4.3.**

Table 4.3 Analytical characteristics of metal ions studied obtained with IonPac CS 5 column.

Metal ion	Linearity range (ng/μl)	Correlation coefficient	Sensitivity (peak area x10^5/(ng/μl)
Pb^{2+}	0.4 - 10	0.9998	43
Cu^{2+}	0.2 - 100	0.9994	1770
Mn^{2+}	0.2 - 80	0.9967	624
Zn^{2+}	0.2 - 80	0.9965	2158
Ni^{2+}	0.2 - 80	0.9981	780

The linearity ranges of metal ions given in **Table 4.3** are seen to cover wide concentration range 0.2-100.0 ng/μl and could be applicable to most of the metal ions studied. Pb^{2+} was the only exception with the linearity in the range 0.4-10.0 ng/μl. It should be noted here that, due to some technical difficulties, linearity cut-off values were not obtained in this work.

The results of the investigation are based on the detection limit, defined as the weight of substance giving a signal twice the standard deviation of the noise level, and the minimum detectable quantity, defined as the amount of sample producing a peak signal two times the noise of metal ions. The obtained chromatogram is shown in **Figure 3.28**. The calculated results are presented in **Table 3.50**. It was found that the detection limits of Pb^{2+} , Cu^{2+} ,Mn^{2+}, Zn^{2+} and Ni^{2+} under the investigated conditions were 0.32, 0.08, 0.15, 0.16 and 0.84 ng, respectively, while the minimum detectable quantities were 1.96, 0.51, 1.33, 2.07 and 37.95 ng.sec, respectively.

The results of reproducibility indicating the precision of analysis are presented in **Table 3.51** (a) and (b). It was found that the relative standard deviations (% RSD) of the metal ion retention times were in the range 0.044-0.315 and those of peak area measurement were in the range1.830-3.430.

The obtained conditions were applied to the determination of metal ions in drinking water samples under the same conditions as the mixture standard solutions. Metal ions found in drinking water samples were Pb^{2+} ,Mn^{2+}, Zn^{2+} and Ni^{2+}. Concentrations of analyte ions were determined from the calibration curves in **Tables 3.52-3.55.** Caibration curves of these metal ions are shown in **Figures 3.29-3.32**. It can be seen that the concentrations of the metal ions in drinking water samples lie between the following ranges : 0.029-0.051 ng/μl for Pb^{2+} , 0.02-0.198 ng/μl for Mn^{2+}, 0.006-0.030 ng/μl for Zn^{2+} and 0.008-0.034 for Ni^{2+}, respectively. Chromatogram of some drinking water sample ($w.w._5$) is shown in **Figure 3.33**.

% Recovery was accomplished with the spike method. The results of % recovery were 97.86 for Pb^{2+} , 98.54 for Mn^{2+}, 99.68 for Zn^{2+} and 98.56 for Ni^{2+} . **Figure 3.34** shows chromatograms of $w.w._9$ sample and $w.w._9$ sample spiked with Mn^{2+}, Zn^{2+} and Ni^{2+} in comparison.

Quantitative confirmation of metal ions in drinking water samples was done by the AAS technique using the external standard method. In order to decide whether there was a significant difference between the results obtained by the IC technique and the AAS technique, the t-test was conducted for the comparison with results shown in **Tables 3.62-3.65**.

The tabulated t value (t_{table}) for six degrees of free freedom at 95% confidence level is 2.571. From the results obtained by the two techniques for Pb^{2+} ,Mn^{2+}, Zn^{2+} and Ni^{2+}, it was found that the calculated t value was smaller than the tabulated t value at 95% confidence level, suggesting that there was no statistical difference in the results by the two techniques.

4.2 Conclusions

In this research anions and cations in drinking water samples were determined using three systems of ion chromatographic techniques, namely, suppressor anion chromatography, suppressor cation chromatography and the post column derivatization. The chemical composition of natural water is generally derived from many different sources of solutes, including gases and aerosols from the atmosphere, weathering and erosion of rocks and soil, solution or precipitation reactions occurring below the land surface and cultural effecting resulting from activities of man. Chemical analyses may be grouped and statistically evaluated by averaging frequency distributions, or ion correlations to summarize large volume of data. The investigation of optimum condition for separation and analysis of anions was accomplished with the IonPac AS 4 A column with 1.80 mM Na_2CO_3/1.70 mM $NaHCO_3$ at the flow rate 2.0 ml/min as eluent employing a conductivity detector at output range 3 μS. The linearity ranges for F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} and SO_4^{2-} were found to be 0.2-200.0, 0.2-400.0, 0.2-20.0, 0.2-100.0, 0.2-100.0 and 0.2-200.0 ng/μl, respectively. The detection limits of these anions were found to be 0.26, 0.17, 0.57, 0.58, 0.88, 0.75 and 0.20 ng, respectively. The relative standard

deviations of peak areas were found to be between 0.76-4.73%. The results of anions in drinking water samples were compared with those from the spectroanalytical technique, based on the t-test. Statistical difference in the results of anions obtained by the two techniques was observed.

In the suppressor cation chromatography, an investigation of optimum conditions for separation and analysis of alkaline earth metals was achieved with the IonPac CS 12 column with 20 mM methansulfonic acid at the flow rate 1.0 ml/min as eluent and 25 mM tetrabutylammonium hydroxide at the flow rate 6.0 ml/min as regenerant with a conductivity detector at output range 10 μS. The linearity ranges for Mg^{2+} , Ca^{2+} and Sr^{2+} were found to be 0.2-100.0 , 0.2-200.0 and 0.2-100.0 ng/μl, respectively. The detection limits of these cations were found to be 0.18, 0.08 and 4.75 ng, respectively and the relative standard deviations of peak areas were found to be 0.460-3.656 %.

The results of cations in drinking water samples were compared with those by the AAS technique. Based on the t-test, there was no sinificant difference in the results obtained from the two techniques.

In the post-column derivatization, an investigation of optimum conditions for separation and analysis of transition metal ions as impurities in drinking water samples was accomplished with an IonPac CS 5 column with 50 mM oxalic acid at pH 5.3, at the flow rate 1.0 ml/min as eluent and $4x10^{-4}$ M 4-(2-pyridylazo) resorcinol in 3 M NH_4OH/1 M CH_3COOH at the flow rate 0.5 ml/min as the post-column reagent with a uv-vis detector at 510 nm. The linearity ranges for Pb^2 , Cu^{2+} , Mn^{2+} , Zn^{2+} and Ni^{2+} were found to be 0.4-10.0, 0.2-100.0, 0.2-100.0 and 0.2-80.0 ng/μl, respectively. The detection limits of

these metals were found to be 0.32 , 0.08, 0.15, 0.16 and 0.84 ng, respectively. The relative standard deviations of peak areas were found to be between 1.830-3.623 %. The results of metal ion analysis by the IC technique were compared with those by the AAS technique. Based on the t-test, there was a statistical difference in the results of the metal ions by the two techniques.