12-1998

# Studies on the Occurrence of Fluoride in Some Food Samples

Taghreed Ali Abdullah Al-Habshi

بسم الله الرحمن الرحيم



United Arab Emirates University
Faculty of Science

# Studies on the Occurrence of Fluoride in Some Food Samples

## A Thesis

Submitted to the Faculty of Science of the United Arab Emirates University in Partial Fulfillment of the Requirements for the Degree of Master of Science in Environmental Science

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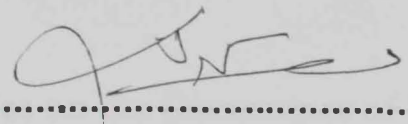
The thesis of Taghreed Ali Abdullah Al-Habshi for the degree of Master of Science in Environmental Sciences is approved .



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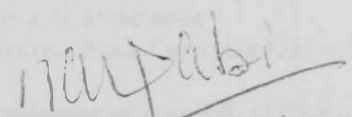
Examining Committee Member, Prof. Tarek Ghonima



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Prof. Abdul Rahman S. Al-Sharhan
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In recent years, the amount of fluoride in biological samples, drinking water and in fluoride containing food or feedstuffs has generated considerable interest. Hence the determination of fluoride is becoming increasingly important due to its implications for environmental health. Fluoride is considered to be amongst the most phytotoxic of the more common pollutants. In response to that extensive research has been made to improve the determination of trace amounts of fluoride through developing different analytical methods. The application of these various analytical methods for fluoride ion determination in water and food samples has gained an enormous interest.

Chapter I of this thesis involves the major aspects of fluoride including availability of fluoride in the environment, physiological effect and mode of action of fluoride. Also it contains a literature survey on the application of various analytical methods of analysis for fluoride ion determination in many of environmental samples.

The experimental part of the thesis is presented in Chapter II. It includes the chemicals, materials and the method of preparation of the various solutions used. The preparation of the different samples for analysis, the methods of analysis as well as the instruments of analysis are described. Moreover, this chapter includes the general standard procedures and techniques established for fluoride ion determination in the environmental samples.

In Chapter III, the results of fluoride ion analysis in the different types of water, tea, honey, juice, dates, spinach and hamour fish were listed. In this context the results indicate that the average value of $F^-$ content in the bottled water was 0.103 mg/L which is relatively lower than the corresponding value in well water. The $F^-$ was not detected in desalinated water whereas in the holy Zamzam water it is close to 0.4 mg/L. The $F^-$ content in tea is 2.33 mg/L and tea could be considered as a good natural source of $F^-$. Also spinach and hamour fish samples could be considered as moderate sources of $F^-$. However, honey, juice and dates contain trace amounts of $F^-$.

Chapter IV describes the application of a spectrophotometric method for the determination of $F^-$ in commercial samples. The method depends on the use of Zr(IV)-thiazolyl azo rezorcinol (TAR) system as a spectrophotometric reagent for fluoride ion determination. The results show that the lower detectable concentration of $F^-$ using this method was $1x10^{-5}$ mol/L of $F^-$. The method was applied for the determination of $F^-$ in commercial mouth wash solutions and the results agreed (about 98.3%) of its content shown on the label of the mouth wash solution bottle.

Chapter V summarizes the results of analysis of $F^-$ in the various drinking water types and different food samples and recommended the fluoridation of the desalinated water. However, the desalinated water has different uses other than its use as a drinking water, therefore we are recommending the fluoridation of the bottled water.

# ACKNOWLEDGEMENT

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I wish to express my sincere acknowledgement to Prof. Dr. Abdul Rahman S. Al-Sharhan, Dean of the Faculty of Science, U.A.E. University, for offering the chance to join the Environmental Sciences Master Program.

I would like to thank the Head of the Chemistry Department, Faculty of Science, U.A.E. University. Thanks are due to Prof. Dr. Mohammed Tarek Ghonima, Professor of Analytical Chemistry and Coordinator of the Environmental Sciences Mater Program, Faculty of Science, U.A.E. University for his encouragements .

I would like to thank the thesis advisors Prof. Dr. Abdel Majeed Kiwan; Prof. Dr. Mostafa M. Kamal, Chemistry Department, Faculty of Science, U.A.E. University and Dr. Mutwakil M. Ahmed, the Quality Manager, Head of Chemistry Unit at Food and Environment Control Centre (FECC), Abu Dhabi Municipality, for their suggestion of the project of the research. Special thanks to Prof. Dr. Mostafa M. Kamal for being very patient and so kind throughout the period of the study and preparation of the thesis.

I would like to thank his Excellency Saeed T. Al-Mazroui, Assistant Under Secretary of Abu Dhabi Municipality for providing the chance to join the Environmental Sciences Master Program at U.A.E. University as well as use the facilities available at FECC.

I would like to express my gratitude to Dr. Amin M. Yousuf, Director of FECC for his everlasting support and continuous encouragement ever since I joined the centre. Much thanks to Eng. Hassan S. Al-Katheri, Head of Laboratories and Specifications at FECC for his genuine advice and guidance.

Many thanks go also to Mr. Abdullah Al-Hammadi, Head of Environment Protection Section, FECC for being very understanding during my research. Thanks to Eng. Farid J. Al-Madani, Head of Central Support Services and Mr. Yousuf Al-Zaabi, the Security Officer at FECC.

I am extremely grateful to my colleague Samia Abdellatif Hassan, the training officer at FECC for the continuous guidance and encouragements which enlightened my carrier throughout the years since I met her. It is worth mentioning that I am deeply indebted to Mr. Mohammed O. Hashim, Technician in Charge and Safety Officer at FECC for his assistance during the study by his faithful knowledge contribution, as I can not forget the cooperation and help offered by Kasim Sulaiman and Abdul Rahman F. Taha at Water and Minerals Group, Chemistry Unit, FECC, in addition of the cooperation I found from Mrs. Amal Al-Tijani, the Librarian at FECC.

I would like also to thank my colleagues at Chemistry and Microbiology Units, Laboratories Section and Environment Protection Section at FECC for their genuine support. My acknowledgement extended to Mr. Arif, Vichn, Barshuman and Jawid for their great help. My deep appreciation to Eng. Louai A. Al-Habshi for the great effort he offered in helping me with the preparation of all the graphs and tables as well as all his help with the computer work during the years of study.

## NOTE

Besides the work carried out in this thesis, the candidate Taghreed Ali Abdullah Al-Habshi pursued postgraduate studies for the partial fulfillment of the M.Sc. degree in Environmental Science in the following topics:

A. Core Courses:

Environmental Science I

Environmental Science II

Environmental Law

Social Impact Assessment

Seminar

Applied Statistics

B. Special Courses:

Environmental Chemistry

Selected Topics in Physical Science

Independent Study in Physical Science

Food Contamination

Pesticidal Chemistry

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# CHAPTER I

# General Introduction

## 1.1. Relevant Aspects of Fluorine Chemistry

### 1.1.1. Introduction:

Fluorine was discovered by the Swedish chemist Karl Wilhelm Scheele in 1771, but it was not isolated until 1886, when the French chemist Henri Moissan prepared the gas by electrolyzing potassium fluoride, KF (Collier's Encyclopedia, 1990).

Many countries resort to artificial fluoridation of drinking water if it is originally deficient in fluoride content. World Health Organization has set a guide line value of 1.5 ppm fluoride in drinking water with the recommendation to adjust the concentration to suit local and climatic conditions.

Several years of extensive research from various regions of the world failed to show conclusive evidence that fluoride is an essential element for human nutrition, except for its effectiveness in reducing dental cavities among children. Even the beneficial effects obtained by consuming water containing optimal concentration of fluoride is only 40-60% on a global average. Absolute values of DMF index (defined as the average number of decayed, missing and filled teeth) observed among population consuming water either deficient (<0.1 ppm) or rich (>0.7 ppm) in fluoride were found to vary significantly. This may be due to several factors such as climatic conditions of the area, dental hygiene, food habits of the population etc. Correlation of dental health and fluoride content in drinking water reported from some hot regions was found to be significantly different from that reported from other parts of the world. It

is therefore difficult to recommend a uniform policy on artificial fluoridation of drinking water supplies that can be applied on a universal basis (Al-Mansour, A.H., 1991).

### 1.1.2. The Physiology of Fluoride (Murray, J.J., 1976)

#### *1.1.2.1. Availability of Fluoride:*

Fluorine is the most electronegative of all chemical elements. It has an atomic weight of 18.998 and an atomic number of 9. It is combined chemically in the form of fluorides, chiefly as fluorite ($CaF_2$) commonly called fluorspar, fluoroapatite ($Ca_{10}$ $[PO_4]_6$ $F_6$) or cryolite ($Na_3AlF_6$) Fluorite which is also called fluor may occur in almost any color due to such impurities as Fe and Mn (Collier's Encyclopedia, 1990), it is seventeenth in the order of abundance of elements in the earth's crust. Barth, 1947 estimated that the earth's crust contained 880 ppm. Most studies have shown that the level of fluoride in soil decreases from below upwards, the mean fluoride content varying between 200 and 290 ppm. Fluorine is more abundant (0.065%) than chlorine (0.055%) in the earth's crust (Cotton, F., 1980). Fluoride also occurs in sea water, in concentrations ranging from 0.8 to 1.4 ppm. It is present in nearly all fresh ground waters, though the concentration in some water supplies is very small. The range of fluoride levels in drinking water varies in different parts of the world. In Africa areas it have been reported with as much as 95 ppm in the drinking water; the range in USA is given as 0-16 ppm (WHO, 1970), whilst in England the range is 0-5.8 ppm.

Additional fluorides are widely distributed in the atmosphere originating from the dusts of fluoride containing soils, from gaseous industrial wastes, from the burning of coal fires in populated areas, and from gases emitted in areas of volcanic activity. In a survey of fluoride in the air of some communities in the USA and Canada, concentrations were in the range 0.02-2 $\mu g/m^3$ (WHO, 1996). Thus fluoride, in varying concentrations, is freely available in nature. It is difficult to understand how any form of life, in land, sea or air, evolved and survived unless it was fully able to cope with continuous uptake from its environment. The fluoride content of plants remains remarkably constant whether they are grown in soil with much or little fluoride. It is naturally found in foliage in the range of 0.24-6.35 mg/kg (Singer, L. and Ophaug, R., 1979). Fresh fruit juices contain fluoride in the range of 0.02-0.14 mg/L in non fluoridated water and 0.15-1.48 mg/L in fluoridated water (Singer, L. and Ophaug, R., 1979).

There is no consistent difference in the fluoride content of the soft tissues of fresh water and salt water fish: very little fluoride appears in cow's milk (0.02-0.05 mg/L) (Backer, D. *et al.*, 1974) and the amount is increased only slightly, if at all, by the addition of large amounts of fluoride to the drinking water or grain ration. Human breast milk contains less than 0.2 mg/L. Negligible amounts of fluoride are stored in human soft tissues and these concentrations do not rise with increased levels of fluoride in the individual's drinking water. It is clear that no

serious imbalance can or does exist between the life processes and ordinary amounts of fluoride acquired from the environment.

### *1.1.2.2. Intake of Fluoride:*

Assuming a water fluoride content of 1 ppm, the average intake from all sources in the United Kingdom would be about 3.2 and 3.3 mg per day for men and women respectively. In children aged 5-14 years the intake is 1.2 mg. Fluoride content was determined in different types of food. Certain types of fish, for example dried mackerel and dried salmon, contain large amounts of fluoride (84.5 ppm and 19.3 ppm respectively). Whole potatoes contain 6.4 ppm, F. It was considered that about 0.3-0.5 mg F were provided by the ordinary mixed solid foods of the American adult. In a further study of daily intake of fluoride from food and drinking water containing 1 ppm F, it was estimated that the total daily intake of a 10-12 year old child would be 0.016-0.069 mg per kg of body weight. Thus for a 50 kg person the total daily intake would be 0.8-3.5 mg.

### *1.1.2.3. Absorption of Fluoride:*

Fluoride is readily absorbed into the body. Absorption occurs mainly from the stomach, is passive in nature, and no active transport mechanism is involved. It was demonstrated that 1 mg of fluoride labeled with $^{18}F$ and ingested by two adult humans was rapidly absorbed. The maximum plasma radiofluoride concentration was reached within 60 minutes.

Absorption can also occur from the lungs by inhalation of fluoride dusts and gases. A third and very rare route of absorption is through the skin. Fluoride absorption may occur when hydrogen fluoride is applied to the skin: however, the resulting burn to the skin is more serious than is the fluoride that is absorbed. It is rapidly excreted via the kidney. Human studies have shown that between 20 and 30 percent of an ingested fluoride dose was found in the urine within 3-4 hours.

Soluble fluorides in drinking water will be absorbed nearly completely, regardless of the level of fluoride in the water supply. The question has been raised whether fluoride in milk is as readily available as it is in water. Using $^{18}F$, it was found that at concentrations of 1 and 4 ppm F the absorption of fluoride from milk was slower than that from water, but that the ultimate percentage absorbed was nearly the same whether fluoride was supplied in milk or in water. Tea is a rich natural source of fluoride. Tea leaves were found to contain up to 300 mg/kg dry weight (Slooff, W. *et al.*, 1988 and WHO, 1984) and the average fluoride concentration in tea leaves is approximately 100 ppm. Approximately 90 percent of the fluoride from this source is extracted after infusion, so that the fluoride concentration of the infusion is around 1 ppm F depending on brand, amount used, duration of infusion and type of water used (WHO, 1996). The absorption of fluoride from food depends on the solubility of the inorganic fluorides in the diet and on the calcium content of the diet. If calcium (as calcium phosphates or calcium carbonate) or aluminum compounds are added, the fluoride absorption is markedly reduced to about 50 percent. In such cases the fluoride is bound in a less soluble form and faecal excretion increases.

*1.1.2.4. Excretion of Fluoride:*

Fluoride is excreted in the urine, lost through sweat and excreted in the faeces. It occurs in traces in milk, saliva, hair and tears. The principle route of fluoride excretion is via the urine and the urinary fluoride level is widely regarded as one of the best indices of fluoride intake. Human urinary fluoride concentrations depend on the drinking water concentrations. The urinary fluoride concentration from 1,900 young males from areas where the fluoride concentration in the drinking water varied from 0.5 to 5.1 ppm and has been repeatedly confirmed. Even small amounts, for example 1.5 mg or 5 mg taken in a glass of water, are absorbed and excreted so rapidly that 20 percent of the fluoride can be found in the urine after three hours. Using $^{18}F$, It was found that up to 30 percent of a 1 mg dose was detectable in the urine in four hours. the very rapid rate of excretion is one of the most protective factors in severe fluoride poisoning: usually either death occurs within four hours or the individual recovers. The critical period is short because F is rapidly removed from the blood stream and extracellular fluid via the kidney and because skeletal deposition is extremely rapid.

*1.1.2.5. Storage of Fluoride:*

Fluoride is stored in the hard tissues of the body. It has been detected in every specimen of bone or tooth analyzed. The extent of fluoride uptake in different parts of the skeleton and dentition depends upon the amounts ingested and absorbed, the duration of fluoride exposure and the type, region and metabolic activity of the tissue

concerned. Therefore there is a great disparity in fluoride levels, both between individuals and between different types of mineralized structures. Even within tissues which appear structurally homogeneous, concentrations may vary markedly over distances of only a few microns.

### *1.1.2.6. Uptake of Fluoride in Hard Tissue:*

The incorporation of fluoride slightly alters the chemical composition of bone and tooth mineral; the carbonate and citrate contents are lowered and the magnesium level increased; the Ca/P ratio, however, remains unchanged. Fluoride enters the mineralized tissues by replacing certain ions and groups normally associated with hydroxyapatite crystallises. A three-stage mechanism to describe the entry of ions into the apatite crystal lattice, which is considered to be surrounded by a hydration shell. The ionic exchange would occur between fluoride ions and hydroxyl and bicarbonate groups and also with fluoride ions already present in the crystal. Finally, ions present in the crystal surface might migrate slowly into vacant spaces in the crystal interior during recrystallization.

### *1.1.2.7. Fluoride Content of Bone:*

Because fluoride ions are able to enter the hydroxyapatite lattice, fluoride concentration in living human bone builds up slowly with age. It was reported that the specimens of rib cortex which seemed to indicate a linear increase in fluoride concentration with age. Jackson and Weidmann (1959) studied postmortem specimens of rib cancellum and found that fluoride tended to accumulate less readily in older specimens

and stated that a plateau level of fluoride concentration was reached at about the age of 55 years. The value of the plateau level depended on the fluoride intake: in West Hartlepool where fluoride content in drinking water is 1.5-2.0 ppm, the plateau level was 4000 ppm, whereas in Leeds ($F^-$ in drinking water is 0.1 ppm) the plateau level was 2000 ppm.

The distribution of fluoride within bone is not uniform. It is highest in those areas of most active growth; for example endosteal and periosteal surfaces usually have a higher fluoride content than the central parts of compact bone (Weidmann and Weatherell, 1959). The two main facts arising from the literature are, firstly, fluoride content of bone increases with age and, secondly, fluoride content of bone increases with increasing fluoride concentration in the drinking water.

*1.1.2.8. Fluoride Content of Enamel and Dentine:*

Fluoride uptake in dental tissues also increases with age and with increasing fluoride concentration in the water supplies, but the fluoride content of dentine and enamel is considerably lower than that found in bone from the same individual. Jackson and Weidemann (1959) showed that in human premolar enamel from West Hartlepool (F = 1.5-2.0 ppm) fluoride concentration increased from 170 ppm F at 10 years and reached a plateau level of 350 ppm at 30 years of age. In contrast, human premolar enamel from Leeds (F = 0.1 ppm) contained 50 ppm F at 10 years and reached a plateau level of 100 ppm F at 30 years of age.

### *1.1.2.9. Fluorine as an Essential Mineral Nutrient:*

In man, the following statements have been made on the importance of fluoride as a mineral nutrient. The Food and Nutrition Board, National Research Council (1974) and WHO include fluoride in their recommended dietary allowances, concluded that extensive medical and public health studies have clearly demonstrated the safety and nutritional advantages that result from fluoridation of the water supply (American Academy of Pediatrics, 1972). The Food and Nutrition Board recommended fluoridation of public water supplies in areas where there are low natural fluoride levels.

The Federal Register of the United States Food and Drug Administration concerning the nutritional labeling of food and dietary supplements, lists fluorine as an essential nutrient, and the report by a WHO Expert Committee on Trace Elements in Human Nutrition (WHO, 1973) includes fluorine in its list of 14 trace elements which are believed to be essential for animal life.

## 1.1.3. Mode of Action of Fluoride in Reducing Caries:

It is possible to explain the systemic action of fluoride on caries as being due to a stabilization of the apatite lattice. Such stabilization is a result of hydroxyapatite having inherent voids due to missing hydroxyl groups. Fluoride ions fill these voids and add their hydrogen bonding tendency to the forces which hold the crystal together.

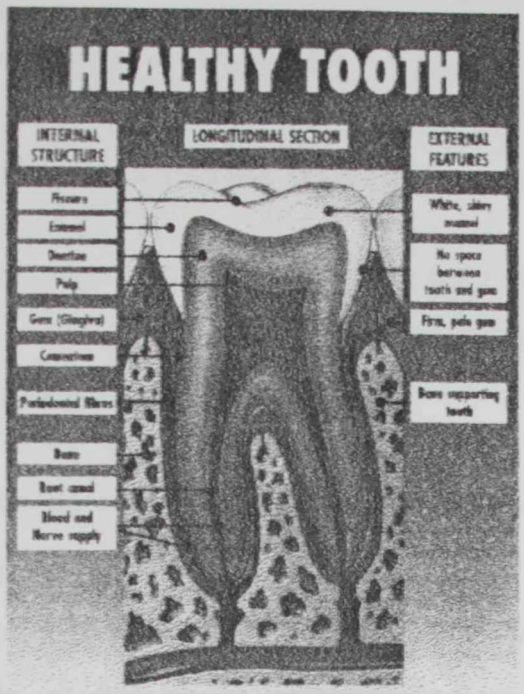
The practical issue is whether the fluoride intake from concentrations known to be effective inhibiting caries (1 ppm F in drinking water) produces sufficiently large differences in the fluoride concentration of the enamel to affect its solubility. The solubility of the intact outer enamel of groups of teeth from towns with water supplies containing 0, 1 and 2 ppm F was compared; all the results showed a trend toward lesser solubility in teeth from the 'high fluoride' areas, but not all the differences were statistically significant. Layers of enamel ground off teeth formed under various fluoride intakes were studied and it was found that enamel with the higher fluoride concentrations was less soluble, but the differences were small and there were some anomalous findings. Jenkins (1970) concluded that, taken as a whole, these results give general support to the theory that fluoride acts by reducing the solubility of enamel, although they are indecisive because there are no means of knowing whether these small and erratic differences are large enough to influence caries.

### *1.1.3.1. Dental Plaque-Enzymatic Inhibition by Fluoride:*

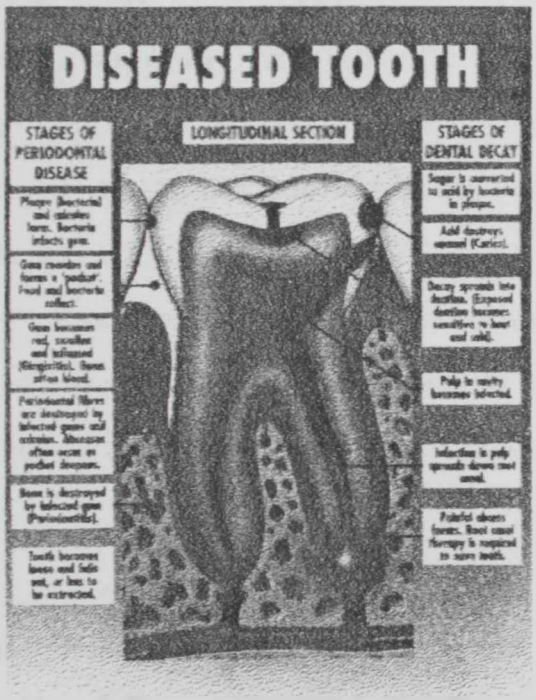
A further important property of the fluoride ion is its ability to inhibit enzyme action and so exert a direct effect on plaque bacteria. (Dental plaque is a soft, tenacious bacterial deposit suspended in a protein matrix which forms on the surface of teeth. It also contains varying amounts of extracellular polysaccharide and desquamated epithelial cells). Depending on the fluoride concentration available, fluoride may reduce the ability of plaque flora to form acid and polysaccharides from

carbohydrates, or it may bring about a change in the microbial composition of plaque. Several investigators have shown that small amounts of fluoride ions (1-10 ppm) will decrease acid production by pure cultures or by saliva-glucose mixtures. Higher levels of ionic fluoride (above 32 ppm) are required to reduce acid production by plaque suspended in buffer.

The protective effects of fluoride against caries (Fig. 1.1) have been observed only at a total dietary fluoride intake of 1.5 mg/day or more. A range between 1.5 and 2.5 mg in adolescents and between 1.5 and 4 mg in adults has been proven safe in a number of studies (Beap, 1971). Higher intakes, such as might be expected in areas with water of a natural fluoride content of 2 or more mg/liter, produced mottling of the teeth in children, a condition of cosmetic concern but of no health importance. Still higher fluoride exposures, for example in an area with drinking water containing 4 mg/liter fluoride naturally, may afford protection against osteoporosis in adults. The well-defined chronic fluoride toxicity, fluorosis, is seen only in persons consuming in excess of 20 mg/day over extended periods of time (WHO, 1970, National Research Council, 1980).




(A)




(B)

Fig. 1.1 A picture of a healthy tooth (A) and a diseased tooth (B)

### 1.1.4. Effects of Natural Fluoride Drinking Water on General Health:

Studies of the physiological manifestations in man of long exposure to high fluoride levels have been summarized in Fluorides and Human Health (WHO, 1970). The main conclusions were:

1. No impairment of or effect on the general health status could be detected among persons residing for an average of 37 years in areas where the water supply contains fluoride at the levels of 8 ppm, and no systemic abnormalities or abnormal laboratory findings were observed that might be associated with ingestion of fluorides (Leone *et al.*, 1954, 1964).

2. Prolonged high fluoride intake up to 8 ppm does not affect morbidity or mortality. Studies of mortality from specific causes of death in 32 communities with 1 ppm F in drinking water have been compared with 32 communities with negligible fluoride in the water. Death has rates from heart disease, cancer, intracranial lesions, nephritis and cirrhosis of the liver were reported. No statistically significant differences were found between the mortality rates of the fluoride and non-fluoride cities, either for these five specific causes or from all causes combined.

3. Young males in high fluoride areas fail to reveal a relationship between bone fractures and fluoride exposure and their height/weight figures compare favorably with those of young men in other areas of

the U.S.A., indicating that fluoride exposure does not influence man's growth pattern.

4. The prolonged ingestion of fluorides does not affect thyroid gland size or function in either man or animals.

Martin (1970), in a review of the effect of fluorides on general health, concluded: "By their wide distribution in nature, their inevitable presence in man's food and drink their consequent presence in the tissues of the human body, fluorides from a natural part of man's environment, yet when present in excess they are known to be harmful. However, results have shown that a level of approximately 1 ppm F in temperate climates has no harmful effects on the community. The margin of safety is such that will cover any individual variation of intake to be found in such areas".

## 1.2. Methods of Fluoride Determination

### 1.2.1. The Potentiometric Methods

Fluoride concentration in digests was measured using a $F^-$ ion-selective electrode in subterranean clover tissue. The sealed chamber digestion method was carried out with nitric acid in Teflon chambers at 120 °C for 6 hours gave the highest $F^-$ concentration in the plant material and the highest recovery of added $F^-$ of all methods. Tests on several types of plant material confirmed the superiority of the closed chamber digestion. The superiority of the method is attributed to the complete solubilisation of $F^-$ in the sample and elimination of losses of volatile $F^-$. (Keerthisinge, G. and *et al.*, 1991).

Fluoride ion-selective electrode has been applied for determination of fluoride in water in the presence of organic compounds with higher accuracy (Spadaro, A.C.C. and *et al.*, 1990). A kinetic determination of alkaline phosphates activity of monofluoro-phosphate was reported using $F^-$ selective electrode by Venetz, W.P. and *et al.*, 1990). The influence of the total ionic strength adjustment buffer (TISAB) solution on the determination of $F^-$ in tea leaves using infusion method was studied by (Colina, J.M., 1990).

The performance of six chelating reagents (ethylenediamine-N,N,N`,N`-tetraacetic acid (EDTA); trans-1,2-cyclohexanediamine-N,N,N`,N`-tetraacetic acid (CDTA); N`-(2-hydroxyethyl) ethylenediamine-N,N,N`-triacetic acid (HEDTA); triethylenetetraamine-

N,N,N`,N``,N```,N````-hexaacetic acid (TTHA) dieethylenetriamine-N,N,N`,N``,N``-pentaacetic acid (DTPA); and citrate have been studied for masking zirconium(IV) in the determination of fluoride with an ion-selective electrode. Citrate was not suitable because it produced a prolonged electrode response. The aminopolycarboxylates, DTPA has a much greater masking ability than the others. Using DTPA at pH 5-6, fluoride was successfully determined at a concentration of $1x10^{-5}$ mol $dm^{-3}$ in the presence of up to $4x10^{-6}$ mol $dm^{-3}$ zirconium(IV). The proposed method was applied to the analysis of a number of zirconium(IV) fluoride compounds and $ZrF_4$ based glasses after fusion with sodium carbonate (Yuchi, 1991).

Salem F.B. and Algannam S.M., 1990 have used the $F^-$ selective electrode for measurement the $F^-$ level in many water samples in Saudi Arabia. Also, the $F^-$selective electrode was used for direct determination of $F^-$ in many of biological samples (Nedelijkovic, M. and *et al.*, 1991). A simple and rapid preparation method for the determination of fluoride in biological materials (blood and food) of various origins, was described. The homogenized sample was placed in a plastic diffusion cell and calcium phosphate added, it was then dried at 55 °C and treated with 70% $HClO_4$ and 40% $AgClO_4$. After digestion for 24 h at 55 °C, the fluorides released were fixed on the upper part of a diffusion cell containing a thin layer of NaOH. The analyses of the diffused fluoride were carried out with an ion-selective electrode. The proposed microdiffusion method, without mineralization, enables quantitative separation of the fluoride from the biological samples.

Determination of fluoride in hydrometallurgical zinc-plant processing products and solutions using fluoride-ion electrode was described (Raghavan, R., 1992). Various types of buffers were tested, to find a suitable common buffer for use in analysis of all types of substances generated at the zinc plant. The method involves discomposition of samples either by fusion with sodium hydroxide or by leaching with perchloric acid to bring fluoride into solution. The fluoride concentration is measured directly with a fluoride-specific electrode. In standard addition tests 100% recovery was obtained when a citric acid/sodium nitrate buffer was used.

An ion-selective electrode-flow injection system has been developed with two ion-selective electrodes arranged in parallel in a flow injection system (Lu, R.M., 1992). The system does not contain a conventional reference electrode, and no liquid junction was present. The sample is injected into the two carrier streams alternately and gives a potential response at the electrode. The proposed method was simple and convenient and was applied successfully to the determination of fluoride and nitrate in natural waters, the determination of sodium and potassium in natural waters and the determination of potassium and nitrate in soil extracts.

A simple method for fluoride determination in Spanish vinegars has been developed (Garcia, C., 1992) to provide direct data on dietary fluoride intake from this product. This work describes a potentiometric method that uses a fluoride selective electrode. Three different TISAB

(Total Ionic Strength Adjuster Buffer) solutions have been evaluated and the method of multiple known additions was used. The precision and accuracy of the developed procedure, in terms of variation coefficient (0.74%) and average percentage of spike recovery (99.9%), were adequate. Forty-two samples of Spanish vinegars were analyzed obtaining a range of fluoride content between 0.12 and 1.95-mg $dm^{-3}$ with an average concentration of 0.52-mg $dm^{-3}$.

A comparative study of different buffering solutions was reported (Delgado, M.M.M., 1993) for the direct potentiometric determination of the fluoride content of beverages manufactured on the island of Tenerife beer and soft drinks. The technique used was that of standard additions. The accuracy and precision for each of the solutions tested is expressed in terms of average and standard deviation of recovery percentages. Orthophosphoric acid (0.75 M) stood out as the optimum buffering solution. Potentiometry, preceded by heat-facilitated diffusion with or without incineration of the sample, was used as a reference technique. With the exception of beers, all fluoride in the rest of the beverages was present in unbound ionic form; it is therefore detectable through direct potentiometry.

Fluoride ions were determined (Ciba, L., 1993) in products obtained from industrial wastes in sodium water glass and sulphsoda (the mixture of sodium sulfate and carbonate). The direct potentiometric measurements were performed in the citrate buffered medium.

A simple and reliable double-cell device with three-ion-selective membranes for fluoride determinations in a continuous flow system with an increased slope factor was described by Borzitsky, J.A., 1993. The relative standard deviation for the analysis of environmental waters was 0.01 - 0.03 and the slope factor was 113-44 mV/PF, depending on the fluoride concentration level; the sampling rate was 120 $h^{-1}$.

A flow analyzer with enhanced sampling frequency combining the features of flow-injection and continuous-flow analysis was reported (Borzitsky, J.A., 1993) for $F^-$ determination. Parameters of the analyser were optimized to ensure the highest rate of analysis allowed by the bubble-through flow cell with fluoride-selective electrodes. Fluoride was determined in 0.1 ml water samples with a sampling rate as high as 720 $h^{-1}$ and a relative standard deviation better than 1%.

Gravimetry and indirect complexometry were simultaneously carried out for $F^-$ determination in each single aliquot of a sample solution (Hioki, A. & Kubota, M., 1994). For correcting both the gravimetry and complexometry results, the concentration of fluoride ions left in the filtrate was determined by a fluoride-ion electrode method. The purity of sodium fluoride based on gravimetry (99.94 ± 0.05%) was in good agreement with that based on indirect complexometry (99.93 ± 0.03%) (Hioki, A. and Khubota, M., 1994).

Toumba, K.J. (1993) measured the fluoride content of 12 bottled waters purchased from two leads supermarkets which was determined by both the direct and acid diffusion methods and found to vary from 0.10 - 0.80 mg/l fluoride (i.e. ppm, fluoride). This article shows that bottled drinking waters contain differing concentrations of fluoride. There is no apparent difference between the direct and acid digestion methods for the determination of fluoride concentrations of drinking waters. Hino, T., 1992 applied a method for direct determination of fluoride-ion in mineral spring water using an ion-selective electrode with standard addition method and computer calculations.

Wang, C.Y., 1995 applied a method of measuring the degree of fluorosis in people who work in a fluoride-polluted environment by the determination of fluoride in human hair. The oxygen flask method of decomposing and the addition of auxiliary combustible adhesive paper to the filter paper wrapping the hair sample before ignition, in combination with Gran's multiple addition of fluoride electrode coupled minicomputer are recommended. This method was simple, rapid, and sensitive and hair samples are easy to obtain. It was the same for the results of the analysis of the degrees of fluorosis of workers who work in a fluoride-polluted environment.

The performance of masking reagents, viz., ethylenediamine-N,N,N`,N`-tetraacetic acid, trans-1,2-cyclohexanediamine-N,N,N`,N`-tetraacetic acid, diethylenetriamine-N,N,N`,N``,N``-pentaacetic acid (DTPA) and triethylenetetramine-N,N,N`,N``,N```,N```-hexaacetic acid

(TTHA), was studied (Yuchi, *et al.*, 1995) for the determination of fluoride in the presence of Hf(IV) and Th(IV) using an ion-selective electrode, Hafnium(IV) was effectively masked using an excess of DTPA at pH 6. TTHA was the best reagent for masking Th(IV), while DTPA provided an alternative for fluoride concentrations of <1 x 10-5 mol/L. The masking reaction was rapid and contamination from membrane-dissolution was negligible. Fluoride contents in raw materials of fluoride glasses, viz., $ZrF_4$ and $ThF_4$ were determined.

Methods based on integration of prevaporation and potentiometric detection in a laboratory-made module were proposed by Papaefstathiou and Decastro, 1995 for the determination of fluoride in liquid and solid samples by formation of a volatile product with hexamethyl-disiloxane. The method for liquid samples was developed in a continuous system either by injection or by aspiration of the in-line-formed derivative and features linear determination between 2.5 and 500 μg/mL with good precision and a sample throughout of 20 samples/h. It has been validated and applied to tap water, ceramic industry wastewater, and dissolved fertilizers. The method for solid samples integrates leaching of the target analyze, formation of the volatile derivative, separation, and detection in the laboratory-made module shows figures of merit similar to those of the method for liquid samples, but the sample throughout is 2 samples/h. It has been successfully applied to the determination of fluoride in orange tree leaves.

Procedures for determination of fluoride in plant material employing acid digestion and solution analysis by ion specific electrode (ISE) were compared to alkali fusion (Stevens, D.P., & *et al.*, 1995) using a range of plant materials. The efficiency of the methods were assessed using standard reference plant material (SRM) not previously available for plant $F^-$ analysis. Acid digestion procedures tested failed to obtain the certified value for F in the SRM. This was due to failure of the acids to liberate $F^-$ bound strongly within silicate minerals found in the plant materials. Acid digestion is therefore not recommended for determination of total $F^-$, but could be used to determine labile $F^-$ in plant materials. During investigation of the acid digestion procedures, it was also found that $F^-$ concentrations determined in solution using the ISE are sensitive to solution pH, even at solution pH values, where complexation of $F^-$ with hydrogen ions ($H^+$) can be discounted. It is therefore recommended that both ionic strength and pH of sample and standard solutions be matched when determining $F^-$ concentration in solution using FISE.

Pires, M.A.F. applied the ISE method to determine fluoride content of twelve different brands of tea sold in Sao Paulo, Brazil, supermarkets in 1996. The fluoride content of the infusions ranged from 0.011 to 0.23 mg/L. On average, a person ingests about 0.089 mg of fluoride per day from these teas.

Results were reported by Kazak, A.S. and *et al.*, 1996 for the study of a solid pH electrode as a potentiometric sensor in acid-base titration of fluoride-containing solutions. Galvanic cells with transfer, consisting of the electrodes of interest combined with lanthanum fluoride electrodes were developed for the quantitative determination of fluoride ions. A combined sensor prepared from the above-mentioned pair of electrodes was suggested.

The ability of selected complexing agents to mask aluminum and release fluoride for potentiometric determination in-stream has been assessed by Davey, D.E., 1992. The experimental manifold incorporated a cascade flow cell and comprised two flow paths, the first for conventional flow-injection and the second enabling stopping-flow analyses to be performed. For solutions containing equimolar quantities of Al and $F^-$ at concentrations up to $10^{-3}$ M in each ion, better than 90% fluoride recovery was achieved in 16 s using Tiron. At higher aluminum loading, fluoride was released more slowly, with citrate and DCTA being found to be more efficient than Tiron. At an Al:F ratio of 4:1 ($10^{-3}$ M $F^-$), relative rates for fluoride over a 10 minute period occurred in the following order: citrate > DCTA > Tiron > tartrate > EDTA. Acetate and hexamine buffers, often recommended as components in TISAB formulations, and were as effective as EDTA in releasing fluoride. Using an acetate buffer with citrate as the decomplexing agent slowed this release. Aged Al/F solutions responded almost as quickly as fresh solutions to Tiron and DCTA, with small pH-related effects being observed for solutions 20 days old (Davey, D.E., 1992).

### 1.2.2. Spectroscopic Methods:

Spectrophotometric methods have been widely applied for $F^-$ determination in various samples depending on the absorption of UV/visible radiation by its mixed ligand complexes. Spectrophotometric determination of $F^-$ was applied by Vallvey and others, 1989 using solid-phase spectrophotometry. The method was mainly dependent on the formation of zirconium-xylenol orange $F^-$ ternary complex in solution. Zenki, M., 1989 applied an indirect spectrophotometric method determination of fluoride by FIA using Arsenazo-III-Uranium complex. Bhatt, P.N. and Agarwal, V.K., 1990 described an extraction spectrometric methods for the determination of fluoride using N-phenyl-benzodyroxamic acid. The determination of fluoride in sea water by molecular absorption spectrometry of aluminum monofluoride after removal of cation and anion interferences was reported by Corvillo, M.A.P. and others, 1990. Manzoori, J.I. and Miyazaki, A., 1990 was proposed an indirect inductively coupled plasma atomic emission determination of fluoride in water samples by flow-injection solvent-extraction.

Okazaki, K. and others, 1992, applied a spectrophotometric determination of fluoride-ion with Zirconium(IV) salt of tetraphenyl-porphine trisulfonate. A critical study has been made by Sahu, P., 1992 on the effect of acid concentration and of polymerized and depolymerized zirconyl ions on the formation of ZrO-XO complexes and their stabilities. At an optimum acidity of 0.5-0.6 M hydrochloric acid,

most of the common cations occurring in silicates do not interfere. Maximum colour development is almost instantaneous for depolymerized ZrO-XO complex, but takes a few hours for the polymerized complex, the colour is stable for several hours. The absorbency is highest for the depolymerized ZrO-XO complex and decreases with an increase in polymerization of the zirconyl ions. Dissolved oxides of nitrogen affect the stability of the ZrO-XO complex but can be eliminated with ureas. A simple, rapid and sensitive spectrophotometric method has been worked out for use of this complex in determination of fluoride in silicates, without separation, after fusion of the sample with sodium, hydroxide at 450-550 degrees (XO = Xylenol orange).

A new chemical method was reported by Cobo, G. and *et al.*, 1993 for the determination of total fluoride in complex liquids and suspensions, such as fruit juices, urine, serum and blood. It was based on the formation of the AIF radical in a graphite furnace after *in situ* oxygen-assisted ashing of the untreated sample. The absorbency of this radical is measured at 227.45 nm. The method was relatively easy to use and provides a low detection limit (14 ng/ml) and reasonable reproducibility (5-10%).

A flow injection-spectrofluorometric method has been applied for the determination of fluoride, based on the ability of trace fluoride (Marco, V. and *et al.*, 1993) to increase the rate of formation of a fluorescent Al(III)-Erichrome red B complex in the presence of hexamethylenetetramine. Various chemical and physical variables affecting the reaction and its

kinetics in the flow system were evaluated. The proposed method is very sensitive, with a detection limit of 10 $\mu g\ l^{-1}$ and a linear calibration graph in the range $1x10^{-6}$ - $2x10^{-4}$ M. The method was successfully applied to the determination of fluoride in tap and mineral waters.

A method based on the back-extraction of Th(IV) from thinyltrifluoroacetone its complex in benzene by aqueous $F^-$ followed by Rastogi, R.K., 1994 spectrophotometric measurement of Th(IV), $F^-$ complex was developed for the determination of fluoride. The coefficients of variation obtained are 2.4% and 1.4% in 11 determinations at $F^-$ concentration levels of 1.0 μg/mL.

Complexes of tetravalent metal ions with chromogenic chelating reagents having only one methyliminodiaacetate group ortho to OH group were examined for spectrophotometric or fluorometric determination of fluoride. Zirconium(IV) and Hafnium(IV) were superior to Thorium(IV) as a central metal ion. Three triphenylmethane dyes showed comparable sensitiveness. Although two azo dyes had lower blank values and higher sensitiveness than triphenylmethane dyes, further modification involving enhancement of solubilities is required for practical involving enhancement of solubilities is required for practical use. Zirconium(IV) complex of a new fluorescent reagent derived from sulfonefluorescein showed an increased in fluorescence intensity on the reaction with fluoride. The mechanism of this change in spectroscopic properties was carefully discussed (Yuchi, A., 1995).

Fe(III)-salicylate complex was used for determination of $F^-$ spectrophotometrically. The method is based upon the reaction between fluoride ions and the coloured complex of Fe(III) with methyl salicylate to form the stable, colourless hexafloride complex of iron. The conditions of the method (pH, time and combination ratio) were studied and a standard curve was obtained for 0.01-0.08 g NaF/ml at 525 nm. A study was conducted on interferences with complexing anions of Fe(III), cations that react with fluoride ions and with common ingredients of dosage forms and dental preparations. The method was validated and the results showed good precision (100.6 ± 2.33%) comparable with that of other analytical methods. Good results were obtained in the spectrophotometric determination of fluoride ions in a stomatological gel and in a toothpaste (Sandulescu, R., 1996).

### 1.2.3. Chromatographic Methods:

Ion chromatographic technique was applied for $F^-$ determination in carbonate minerals (Ichikuni and Tsurumi, 1990). Also, it was applied for the determination of urinary fluoride creatinine ratio in monitoring the daily in take fluoride ion (Kertes, P. and others, 1989).

An application of the alizarine complexone (ALC) photometric method using a succinic acid-hexamethylenetetramine buffer (pH 4.6) and ion chromatography (IC) for the determination of fluoride in gypsum has been studied. The sample was decomposed with HCl. For the spectrophotometry, acetylacetone was added to a portion of the neutralized

solution and its absorbance was measured using La-ALC photometry. For IC, after dilution and pretreatment on a column packed with cation-exchange resin of the silver form, the sample agreed well with the values by the JIS method. These methods were rapid and useful (Nakayama, N. and *et al.*, 1994).

Elimination of interferences effect of metal ion in the determination of fluoride-ion by Non-Suppressor Type Ion Chromatography was studied (Tokunaga, S., 1996). By alkalifying $F^-$ solutions at pH 12.3, the metal interference can be eliminated up to the concentrations of 0.25-nM Al(III), La(III) and Y(III); 1.0-nM Ce(IV); 2.5-mM Ce(In); and 5.00-mM Pb(II), Cd(II), Fe(II) and Ni(II). The Ca(II) interference cannot be eliminated. The pretreatment enables determination of 0.2 to 5.0 mM $F^-$ in the presence of 0.25 mM Al(III) or La(III) with coefficient of variations of 1.99 to 6.20%.

$F^-$ was determined to very low detection limit in various environmental samples (Milk and water) using gradient elution ion chromatography and head space gas chromatography (Mizobuchi, 1990 and Tashkova, 1990). An ion-chromatographic method was developed for the determination of trace amount of free urinary fluoride, using an Ods column dynamically coated with cetyldimethyl-n-butylammonium bromide. The many inorganic and organic anions commonly found in urine had little effect on the determination of fluoride (Michigami, V., 1993).

Haldimann, and Zimmerli, 1993 studied the evaluation of ashing procedure for the gas chromatographic determination of fluoride in biological material. Cluster analysis of fluoride yields with the various ashing methods revealed a difference between plant and non-plant materials, using alkaline fusion (KOH) for plant materials and a retaining agent (CaO) for non-plant materials. The combination of both ashing aids gave satisfactory results regardless of the sample type. Applicable of this ashing method to Swiss total diet samples from the year 1983 and comparison with an ion-selective procedure in another laboratory yielded consistent results and identical mean values of 1.9 mg g F $g^{-1}$ (dry matter), corresponding to a daily dietary intake of 0.9 mg $F^-$ per adult.

Vasconcelos and others, 1994 have been used ion-chromatography for determination of fluoride in welding fumes with elimination of high contents of iron by solid-phase extraction. The accuracy of the procedure was evaluated by analyzing both synthetic solutions and real samples. When several mixed standard solutions of fluoride, iron(III) and aluminum(III), covering the ranges and ratios of concentration levels in real samples, were analyzed, practically quantitative fluoride recovery (97-101%) was found.

### 1.2.4. Miscellaneous Methods:

A very sensitive electrochemical method for trace measurement of fluoride in water was reported by using stripping voltammetric technique. The complex of cerium(III) with alizarin complexone (ALC) and fluoride

ion is adsorbed at the dropping mercury electrode. In cathodic sweeps, the peak height is directly proportional to the concentration of fluoride over the range of $8x10^{-8}$ to $5x10^{-6}$ M ($1.5x10^{-9}$ to $9.5x10^{-8}$ g/ml), and the detection limit was $5x10^{-8}$ M ($9.5x10^{-10}$ g/ml). The proposed method was applied to the determination of fluoride in some water samples (Lu, G.H., 1991).

A highly selective and sensitive fluorometric method was described by Tabata, M. and *et al.*, 1994 for determination of the fluoride ion at the parts per billion level via the ion-pair complex formation of the fluoride ion with an expanded prophyrin [2, 23-diethyl-8, 17 bis (2-3 sap)]. The ion-pair complex gives out an enhanced fluorescence intensity at 880 nm on excitation at 450 nm. Since the presence method is based on a direct reaction of the fluoride ion with the sapyrin, a 200-fold amount of the aluminum(III) ion [$10^{-4}$ M (M = mol $dm^{-3}$)] and a 2000-fold amount of the iron(III) $10^{-3}$ M over the fluoride ion did not interfere with determination of the fluoride ion at concentrations as low as $5x10^{-7}$ M in the presence of 1,2-diaminocyclohexane-N,N,N`,N`-teraacetic acid. The proposed method was applied for $F^-$ determination in water, river water, rain water, underground water, and hot spring water and satisfactory results were obtained.

In the presence of fluoride ions, aluminum reacts with N-salicyclideneethylenediamine to form fluorescent Schiff base complexes. A flow-injection analysis system based on this reaction has been developed for a determination of the fluoride ions at the ppm level. By measuring the fluorescence intensities, the fluoride ions could be

selectively determined over the range 0.15 - 10 ppm; 40 samples could be analyzed per hour. The proposed system was applied to an analysis of the fluoride ion in river water (Aoki, I., 1992).

Two titrimetric methods were developed for the determination of fluoride contents in some pharmaceutical preparations used for fluoridation. One of the methods is catalytic controlled-current potentiometry involving two identical platinum indicator electrodes and thorium nitrate as titrant. The reaction between hydrogen peroxide and potassium iodide in the presence of acetate buffer (pH 3.6), which was catalysed by the excess of thorium nitrate, served for the end-point indication. The other method was the automatic potentiometric titration involving a fluoride-selective electrode and lanthanum nitrate as titrating agent. In both procedures, special attention was paid to sample pretreatment and to determination of optimal experimental conditions. Fluoride contents in the range 16-32 μg/ml were determined with a relative standard deviation less than 1.34%. The results were compared to those obtained by standard methods described in the United States Pharmacopeia XXI and recommended by the manufacturer of the preparations (Abramovic, B.F., 1992).

Blatny and Kvasnicka, 1994 have been determined of fluoride in feed mixtures by capillary isotachophoresis. The detection limit, depending on the sample treatment, was as low as 5 μg/g as fluoride. A comparison of the developed ITP method with ion-selective electrode method was carried out.

A sequential flow injection method for simultaneous chloride and fluoride determination in waters with potentiometric detection was described. The method is based on the simultaneous chloride and fluoride potentiometric detection using two ion-selective electrodes in two serial flow-through cells. The necessary ionic strength adjustment is obtained by mixing the TISAB solution with the sample by diffusion during the propelling process to the detection cells. The new method was applied successfully to drinking water samples (Alpizar, J., 1996).

## 1.3. Aim of the Work

Review of a large number of published data from several countries indicate that there is some correlation between dental health and fluoride content in drinking water. In general, it has been shown that water containing fluoride up to an optimal concentration of 1.5 ppm reduces dental caries especially among children, while consumption of drinking water containing excessive fluoride can result in mottling of teeth and dental fluorosis. But several factors need to be considered before either drawing a general conclusion from these observation or in applying it to specific countries or communities.

The so called beneficial effects, i.e. the reduction of dental caries among children consuming fluoridated water, is only partial. On a global average the incidence of dental caries were about 40-60% lower in fluoridated areas in comparison to nonfluoridated areas.

The optimal level of fluoride concentration in drinking water applicable to any given country or community depends on several factors e.g. ambient temperature and food habits of population.

Therefore, the study in this thesis dealt with the occurrence of fluoride in desalinated and bottled water (drinking water), underground water (well water) and in some food samples in UAE. This is done to throw some light on the approximate daily uptake of fluoride by the people who live in this area. Moreover, development of a spectrophotometric method for the determination of fluoride ion in commercial mouth wash solutions was discussed.

# CHAPTER II

# Experimental

## 2.1. Determination of $F^-$ in Water and Food Samples

### 2.1.1. Chemicals and Solutions:

All acid reagents e.g. $HNO_3$, $HClO_4$, HCl were analytical grade (BDH). 0.50 M and/or 20% (v/v) solution of the acid were prepared. The diluted acid solutions were prepared by diluting a specific volume of the stock 0.5 M acid solution to the proper volume. Alkali reagent e.g., NaOH of analytical grade (BDH) was used and 0.10 M was prepared. All solutions were prepared using high purity deionized water with conductivity 0.5-1.5 μs/Cm.

Dionex stock standard solution containing a mixture of five anion standards in deionized water of total volume (100 ml) and it consists of: $F^-$ 20 mg/L, $Cl^-$ 30 mg/L, $NO_3^-$ 100 mg/L, $PO_4^{3-}$ 150 mg/L, $SO_4^{2-}$ 150 mg/L and Dionex stock standard $F^-$ solution 1000 mg/L. Standard solutions with different concentrations were prepared by diluting a specific volume of the standard Dionex solutions to the proper volume. One point calibration and two points (levels) calibration were used during the ion chromatographic measurements.

Combined carbonate - bicarbonate eluent solution 1.8 mM $Na_2CO_3$ (0.191 gm/L), 1.7 mM $NaHCO_3$ (0.143 gm/L). Regeneration of the IC Column was carried out using 25 mN $H_2SO_4$, (3 ml concentrated $H_2SO_4$, specific gravity = 1.84 dilutes to 4 litre with water).

Fluoride standard (NaF 100 ± 0.5 ppm as $F^-$, (Orion application solution), certified traceable to NBS standard reference material for ISE measurements.

**TISAB II:** Total ionic strength adjustment buffer, an improved TISAB containing 1,2-cyclohexylene dinitrilotetraacetic acid (CDTA) instead of citric acid. Addition of this solution to the tested solution will eliminate the interferences effect of $Al^{3+}$ and $Fe^{3+}$ up to 3 ppm in samples containing 1 ppm fluoride (Orion application solution TISAB).

Low level TISAB were prepared and used for analysis of samples containing less than 0.4 ppm fluoride and no fluoride complexing agents such as iron ($Fe^{+++}$) or aluminium ($Al^{+++}$) are present. Low-level TISAB was prepared by placing 500 ml distilled water in a 1 liter beaker, 57 ml glacial acetic acid and 58 gm reagent grade sodium chloride were added. The beaker was placed in a water bath for cooling, a calibrated pH electrode was immersed into the solution, and 5 M NaOH was added slowly until the pH adjusted at 5.0 – 5.5. Solution was cooled to room temperature, and it was poured to 1 liter volumetric flask and diluted to the mark with distilled water.

Orion reference electrode filling solution 90-00-01 saturated with AgCl was used. Orion standard filling solution and prepared filling solution (1 M $KNO_3$) for the fluoride combination electrode were used. 1 and 10 ppm fluoride/TISAB standards (Orion solutions) were used for electrode efficiency.

Sodium fluoride (NaF) powder (BDH) was used for preparing 100 ppm fluoride standard stock solution. Solutions with different concentrations were prepared by diluting specific volumes of the 100 ppm fluoride stock solution and mixed with $HClO_4$ acid solution to the proper volumes. The latter solution was prepared for electrode calibration used in spinach samples measurements.

Solution containing 0.5 gram EDTA (disodium salt) and 0.5 gram Triton-X-100 per litre water was prepared as a washing solution for plant tissues (Spinach leaves).

Sodium acetate (BDH) was used in preparing 15% sodium acetate solution which is required for the neutralization of sample's acidic solutions when measuring $F^-$ using the fluoride ion selective electrode.

## 2.2. Samples Under Investigations

### 2.2.1. Water samples:

Water samples from three different sources were used for this study.

#### *2.2.1.1. Bottled water:*

Various types of bottled water of different volumes and sources were selected from Abu Dhabi markets and from the produced company itself, Al-Ain Water (Al-Ain), Massafi (Ras Al-Khaimah), Gulfa (Ajman), Al Waha (Abu-Dhabi), Falcon Spring (Um Al-Quwain), Awafi (Ras Al-Khaimah), Super Gulf (Um Al-Quwain), Emirates (Fujairah), Jeema (Dubai), Tanuf (Oman), Perrier (France), Evian (France), Volvic (France), High Land Spring (Scottland), Aqua Idka (Slovakia), Zamzam Water (Makka), hand delivered.

#### *2.2.1.2. Desalinated water:*

Desalinated water samples were taken from the samples brought to the laboratory for routine analysis. The samples were collected from Shahama, Marfaa, Wathba, Baniyas and from Abu Dhabi.

#### *2.2.1.3. Under ground water:*

Underground water samples were collected from farm wells of different locations in Liwa, the western region of Abu-Dhabi Emirate.

### 2.2.2. Tea samples:

Various types of tea bags and tea leaves of different batches were collected from supermarkets of Abu Dhabi such as Lipton (tea bags), Brooke Bond (tea bags), Al Wazza (tea bags), and Leone (tea leaves).

### 2.2.3. Juices samples:

Various types of "Lacnor" brand juices of different batches and volumes were collected from the supermarkets of Abu Dhabi for example Apple, pineapple, cocktail, mango, orange, grape, apricot, guava.

### 2.2.4. Honey samples:

Different samples of honey from Sudan, Saudi Arabia, Yemen, and from Germany (Langenese brand) were analysed.

### 2.2.5. Spinach samples:

Fresh spinach samples of two different sources were collected from the local market, Omani and Ras Al Khaimah spinaches.

### 2.2.6. Date sample:

One type of wrapped date, (Lulu) type of local source from different batches were collected from the supermarket.

### 2.2.7. Fish samples:

Different weights of hamour fish were collected freshly from the local market.

## 2.3. Instruments

### 2.3.1. Chromatographic measurements for water samples.

Ion chromatograms were recorded using Ion Chromatograph system (IC) of Dionex model using the following specifications:

- Dionex quaternary gradient pump.
- Dionex conductivity detector.
- Dionex advanced chromatography module.
- Dionex autoion 100 controller.
- HP 3396 series II integrator.

IC was settled up according to manufacturer's instructions (Dionex instruction manual), and the instrument parameters were adjusted according to the following recommended operating conditions (Dionex cook book).

Compressed nitrogen gas : high purity 99% (40 psi)

| | | |
|---|---|---|
| Sample loop volume | : | 50 µL |
| Guard column | : | HPIC - AG4A (Dionex Cat. No. 43175) |
| Separator column | : | HPIC - As4A (Dionex Cat. No. 43174) |
| Eluent flow rate | : | 2.0 ml/min |
| Suppressor | : | Anion Micromembrane (Dionex, MMS-1, Cat. No. 38019) |
| Regenerant | : | 25 mN $H_2SO_4$ |
| Regenerant flow rate | : | 3 ml/min |
| Detector setting | : | 3 µS |

### 2.3.2. Potentiometric measurements:

Fisher Scientific - Accumet 950 (electrometer) pH/ion meter was for various potentiometric measurements (pH and pF). For $F^-$ determination the electrometer was coupled with ASI fluoride combination electrode, a solid state ion-selective electrode (ASI P/N RF 001925) or Russel/pH limited ISE 94-4099 fluoride electrode and Orion research incorporated reference electrode No. 900100. For pH measurement a Fisher Scientific pH electrode was used.

### 2.3.3. Inductive coupled plasma emission spectrophotometer (ICP-ES) measurements:

The cations concentration levels in the various investigated samples were measured using Inductively Coupled Plasma (ICP) plasma 400 emission spectrometer "Perkin Elmer" equiped with PE autosampler and PC data station.

### 2.3.4. Drying processes, Drying oven, Fisher Scientific Iso temp oven, model 655 G:

Drying oven, thermolyne oven and microwave oven CEM MDS-8ID with capping/decapping station, CEM corporation, USA were used for drying the investigated samples e.g. Spinach and fish.

## 2.4. General Procedure for Quantitative and Semiquantitative Determination of $F^-$ in the Investigated Samples

Various procedures were used for quantitative determination of $F^-$ in a wide variety of samples. The procedure for each sample was selected according to the nature of sample and the sample preparation step before determination. These procedures could be classified as follows:

### 2.4.1 a. Determination of $F^-$ in water using IC: (APHA, 1981 and Dionex IC Methods, 1987).

After setting up the IC system and adjusting the instrumental parameters according to the recommended operating conditions as mentioned in 2.3.1, and after allowing system to run. The eluent was pumped through the columns until stable system pressure is obtained (approximately 15-20 minutes). A calibration was done by one point and two points (levels) calibration using a mixture of anions ($F^-$, $Cl^-$, $NO_3^-$, $PO_4^{-3}$, $SO_4^{-2}$ as specified below:

| Std. | Minimum level (mg/L) | Maximum level (mg/L) |
|---|---|---|
| $F^-$ | 0.2 | 2.0 |
| $Cl^-$ | 0.3 | 3.0 |
| $NO_3^-$ | 1.0 | 10.0 |
| $PO_4^{-3}$ | 1.5 | 15.0 |
| $SO_4^{-2}$ | 1.5 | 15.0 |

One and two points calibration (0.1, 0.2 ppm) were used in cases of water samples containing $F^-$ less than 0.2 ppm. Instrument detection limit is 0.06 ppm for $F^-$, when measuring water samples, area counts obtained from the peaks of the separated anions are multiplied by the slope of the calibration curve, slope is the response factor which is amount/area of the calibrated peaks.

Dilutions were made in case of high concentration of salts in some bottled water, underground water including Holy Zamzam water, and dilution factor is considered. Spiking with $F^-$ standard was made in case of samples containing very low concentration of $F^-$ and in case of overlapping of peaks when interferences occurred at $F^-$ retention time as in Holy Zamzam water and perrier bottled water.

All the listed values of the concentration level of $F^-$ and other anions are the mean values of the replicated measurements.

**2.4.1 b. Determination of $F^-$ in water samples using fluoride ion selective electrode (FISE):**

$F^-$ electrode operation (slope) was checked before calibration steps and measuring the $F^-$ level in the samples under investigation. Two point calibration was done (0.1 - 1.0 ppm $F^-$), (0.2 - 2.0 ppm $F^-$), (0.5 - 5.0 ppm $F^-$) and (1.0 - 10.0 ppm $F^-$) were applied for calibrating of the FISE. All of these two point calibration give an acceptable slope (very close to 59 mV) and the electrode detection limit is Ca 0.02 ppm $F^-$ (Orion, 1991).

After calibration of the electrode the samples were measured by adding equal volumes of samples and TISAB II (low level TISAB was also used). Stirring thoroughly using magnetic stirrer, dipping the $F^-$ electrode and waiting until stable reading was obtained on the screen of electrometer. This reading is the water $F^-$ concentration in mg/mL which was taken directly. Known addition technique was used to verify the results of a direct calibration or to measure the total concentration of the F ion in the presence of a large excess of a complexing agent, the sample potential is measured before and after addition of a standard $F^-$ solution, the following equations are used in determining the original sample concentration:

$$Q = \frac{P}{[(1+P)^{DE/s}]-1}$$

where $Q$ = corresponds to the change in potential, DE.

$DE = E_2 - E_1$

where $E_1$ = electrode potential before addition of $F^-$ std.

$E_2$ = electrode potential after addition of $F^-$ std.

$S$ = electrode slope

$$P = \frac{\text{volume of std.}}{\text{volume of sample}}$$

The sample original concentration is obtained by:

$$C_{sample} = Q \times C_{std.}$$

where $C_{sample}$ = sample concentration

$C_{std.}$ = standard concentration

$F^-$ standard volume used in the known addition technique was 10% of the total volume of the mixing sample and TISAB) (Orion, 1991). In case of underground water, filtration was done to remove the suspended particulate and for some desalinated water as well before measuring.

All the listed concentration levels of $F^-$ are the mean value of the five replicated measurements.

**2.4.2 a. Fluoride determination in tea using Ion Chromatography:**

Infusion procedure for sample preparation of infused tea was followed for the determination of infused fluoride from tea leaves. Calibration of IC of Dionex model is done using one point calibration of a mixture of "Dionex Standards" consists of $F^-$, $Cl^-$, $NO_3^-$, $PO_4^{-3}$ and $SO_4^{-2}$ and their concentrations were 2, 3, 10, 15 and 15 ppm respectively.

Then about 50 µL (0.05 ml) of prepared tea sample is loaded into IC instrument through the injection port letting the previous anions to be retained which will appear through the chromatograms. It is noticed that a large peak comes in the retention time of fluoride ion.

To check whether only fluoride ion has been separated at that retention time or other organic ions (acetate ion) have interfered, 1 ppm $F^-$ std has been injected which shows a specific peak height, then 1 ppm $F^-$ std has been spiked with 15% of sodium acetate (0.05 ml of 15% sod. acetate + 9.95 ml of 1 ppm $F^-$ std.) when injected, a peak of double height is

obtained in exactly the same retention time of F ion which are shown from the chromatograms. The other anions ($Cl^-$, $NO_3^-$, $PO_4^{-3}$, $SO_4^{-2}$) are separated without interferences.

**2.4.2 b. Fluoride determination in tea using $F^-$ selective electrode (Colina, 1990):**

2.0 gram of a tea bag (a representative sample of the four different tea brands) was placed in a conical flask (125 ml). 100 ml of boiling deionized water was added with stirring and stayed for 5 minutes infusion time followed by filtration. An equal volume of the prepared tea solution and TISAB II were mixed for $F^-$ determination using FISE. Electrode operation (slope) was checked before the measurements. The $F^-$ electrode was dipped in the stirred solution for some time until stabilization of the reading on the meter screen. Reading obtained from the meter is the concentration of fluoride in tea in ppm (mg/L) that is converted to mg/kg by:

$$\text{mg/L} \times \frac{\text{Total volume (100 ml)}}{\text{Wt. of tea leaves (2 gm)}}$$

TISAB II is added to prevent any complexing agents ions as $Al^{3+}$ or $Fe^{3+}$ that may complexes with fluoride ions, this TISAB eliminates up to 3 ppm of $Al^{3+}$ or $Fe^{3+}$ that might be present in the sample solution and it buffers the sample solution and adjust the pH to become from 5-6 and it controls the total ionic strength of both the standard and the sample (total ionic strength of the sample solution does affect the fluoride measurement by the $F^-$ electrode because of the interferences of some

other ions especially when the sample contains highly dissolved salts) which affect the solution's ion activity that affects the electrode potential (Orion, 1991).

**2.4.2 c. Effect of infusion time on the extracted $F^-$ from tea:**

4 gm of a representative sample of Lipton (tea bag) were weighed in a conical flask. 200 ml of deionized boiling water was poured into the flask and well mixed, then after 1 minute infusion time, 25 ml of the infused tea solution was filtered using a filter paper into 25 ml of a measuring cylinder, which was then mixed with same volume of TISAB II in a 50 ml beaker followed by measuring using FISE. After 1, 3, 5, 8, 11 and 15 minutes respectively same procedure was followed and the readings were listed. Readings obtained from the meter were in mg/L which were converted into mg/kg and mg/tea bag.

$$\text{mg/kg} = \text{mg/L} \times \frac{200 \text{ ml (total volume)}}{4 \text{ gm (weight of sample)}}$$

$$\text{mg/tea bag (2 gm)} = \frac{\text{mg/kg}}{500}$$

The listed concentration levels of $F^-$ are the mean value of 4-5 replicated measurements.

**2.4.3. Analysis of juices samples:**

50 ml of the well shaked juice sample was mixed with the same volume of TISAB II in a 150 ml beaker and boiled for two minutes (Skog,

1993). The mixture solution was transferred into 100 ml measuring flask and it was completed till mark with deionized water and volume was divided into 5 volumes of 20 ml each. Each volume was placed in a 50 ml beaker and was subjected to the calibrated FISE. The average value of the five readings were recorded. 50 ml of deionized water instead of juice sample was mixed with same volume of TISAB II and the corresponding $F^-$ concentration levels were measured by FISE and the average value of the 5 readings was considered as a blank. The Fluoride concentration in mg/L and mg/200 ml were calculated by:

$$\text{Conc. of } F^- \text{ (mg/L)} = \frac{\text{(juice reading - blank reading) x Total juice volume (50 ml)}}{\text{Volume of juice taken (50 ml)}}$$

$$\text{Conc. of } F^- \text{ in mg/200 ml (package)} = \frac{F^- \text{ conc. in (mg/L)}}{5}$$

Cations were measured either directly in the clear juice as apple juice or mixing 1 ml of juice sample with 9 ml of $HNO_3$ acid solution of different concentration (2%, 5% or 20%) depending on the juice texure results were obtained in mg/L (Egan, H. and *et al.*, 1981).

$$\text{Cation conc. in juice (mg/L)} = \frac{\text{reading from ICP (mg/L) x Total volume (10 ml)}}{\text{Juice volume taken (1 ml)}}$$

Anions were not detected through the Ion Chromatograph system due to the acidity of juice samples that may damage the separating column which is of organic type. Many trials were applied to neutralize the acidic juice media by mixing with $CO_3^{-2}/HCO_3^-$ mixture solution (eluent soln.) trying to measure the $F^-$ conc. using the IC. The listed Fluoride ion concentrations are the mean values of five replicated measurements.

**2.4.4. Analysis of honey samples:**

10 gm of honey sample was weighed in a beaker of 250 ml, then dissolved in 50 ml of deionized water. The honey solution was mixed with same volume of TISAB II and boiled for 2 minutes, followed by transferring completely into 100 ml volumetric flask and completed till mark with deionized water. The whole volume was divided into five volumes of (20 ml each) in 50 ml beaker and measurement were carried out using FISE. pH of the mixed honey solution and TISAB II was adjusted between 5-6. Blank was measured by mixing pure deionized water with TISAB II following the same procedure and measurements (Skoog, 1993).

Average readings were calculated from the five groups of both honey sample and blank and results obtained are calculated as:

Conc. of $F^-$ in honey sample (mg/kg) =

$$\frac{\text{honey average reading (mg/L) - blank average reading (mg/L)}}{\text{Weight of honey sample (gm)}} \times \text{Total honey soln. volume (50 mL)}$$

Cations were measured from prepared honey solutions using ICP and results obtained in mg/L (Egan, H. 1981). Honey solution prepared for the detection of anions ($Cl^-$, $NO_3^-$, $PO_4^{-3}$, $SO_4^{-2}$) and cations was carried out by dissolved 2 grams of honey sample in 50 ml or 100 ml of deionized water in a measuring flask (Egan, H. 1981) and concentration of each anion in mg/kg was calculated as follow:

$$\text{Conc. in mg/kg} = \frac{\text{Conc. in mg/L (reading from IC) x Total volume}}{\text{Weight of dissolved honey sample (gm)}}$$

Anions ($Cl^-$, $NO_3^-$, $PO_4^{-3}$, $SO_4^{-2}$) concentrations were obtained by injecting 50 µL (0.05 ml) of honey solution using a syringe of 10 ml volume into the Ion Chromatograph system through the injection port, after separation and peaks area counts were obtained, calculations were carried out as in 2.4.1a. (calibration was done before measuring samples as in 2.4.1a) (In house SOP). All the reported concentration levels of $F^-$ and other anions are the mean value of five replicated measurements.

**2.4.5. Determination of fluoride ion in spinach:**

500 g from two sources of fresh spinach were placed in a plastic container separately and washed using the plant tissue wash solution for 30 seconds with gentle agitation (all plant leaves with sticks). Plant tissues were drained from water for a few seconds using sieve, then rinsed for 10 seconds in each of three containers of water. The plant tissues were dried in paper towels to remove excess water, then placed in oven for drying at 85 °C for 24 hours. Dried plant tissues were powdered and placed in a labeled polypropylene container with moisture-proof seal.

A 0.5 gram of well-mixed sample was placed in a polypropylene or polyethylene containers and 25 ml of (0.1 N $HClO_4$) was added and closed securely with a screw cap and placed in a water bath at 80 °C for 4 hrs. with shaking every 10 minutes. Blank solution was prepared in a similar manner and placed at the same conditions in a separate container. An additional 25 ml (0.1 N $HClO_4$) was added to each of the containers and well shaked, 50 ml volume of TISAB II was added to each container and mixed again. The sample in each container containing 100 ml of mixed

sample solution and TISAB II including the blank was divided into five groups of 20 ml each. Each 20 ml was subjected to a calibrated FISE and the average value of the 5 readings were recorded (ASTM, 1997). The fluoride electrode calibration was done using 0.2 ppm and 1 ppm $F^-$ std. Fluoride concentration in the spinach sample was calculated as follow:

Conc. of $F^-$ in mg/kg =

$$\frac{\text{Average sample readings (mg/L) - Average blank readings (mg/L)}}{\text{Weight of the dried sample (gm)}} \times \text{Total spinach solution volume (50 mL)}$$

Standard addition method was used to determine the fluoride content in the Omani spinach sample after treatment and preparation, the treated sample solution was divided into four volumes of 20 ml each, 2 ml of deionized water, 2 ml of 0.1 ppm, 2 ml of 0.2 ppm and 2 ml of 0.4 ppm of standard fluoride (Orion solutions) were added respectively to the four volumes of sample solutions. FISE was used for measuring the mV (potential) after spiking the sample solution. The values of mV were plotted versus $\log \frac{1}{[F^-]}$.

A graph was drawn from which the fluoride original concentration in the Omani spinach sample was calculated as follows:

$$\frac{0.02628 \text{ mg/L (from graph)} \times 50 \text{ ml (T.V)}}{\text{Weight of sample (gm)}} = \text{mg/kg}$$

The reported $F^-$ concentration in the two samples are the mean values of three replicated measurements.

**2.4.6. Determination of Fluoride ion in dates:** (Keerthisinghe, G., 1991)

The packaged date was converted to paste form, and dried in a drying oven, then about 5 grams of the dried date sample was weighed in a Teflon vessel, 25 ml of 10% $HNO_3$ acid solution was added for wet ashing (acid digestion), and placed in a microwave oven which was adjusted at 25% power for 3 minutes, followed by 5% power for 10 min and 15% power for 5 min. When the vessel was cooled it was rinsed properly with deionized water and the solution was transferred completely into 100 ml volumetric flask through a filter paper until reached up to mark. A blank was prepared in the same procedure but without sample. The sample solution and blank were measured. Checking of electrode operation (slope) was carried on, then calibration was done using 0.2 ppm $F^-$ and 2 ppm $F^-$ with 15% sodium acetate as a neutralizing agent that must be added to both the standard and sample's solutions to maintain the same ionic strength in both solutions. The pH of the sample solution and the blank solution is close to 1.0, this pH is less than the range at which the fluoride ion electrode acting (pH 5-6). To neutralize the solution a sodium acetate solution was added to the sample or blank solution. After neutralization with sodium acetate and mixing with equal volume of TISAB II, solutions pH becomes about 5.2 and the solution was ready for measuring. Fluoride concentration in date sample was calculated as follow:

$F^-$ conc. in mg/kg =

$$\frac{\text{Average sample readings (mg/L) - Average blank readings (mg/L)}}{\text{Weight of sample taken (gm)}} \times \text{Total volume of the digested date solution (100 mL)}$$

### 2.4.7. Analysis of hamour fish samples:

Two different weights of hamour fish were collected freshly from the local fish market (1.5189 kg and 1.2432 kg).

### 2.4.7 a. Sample preparation:

Tissues (muscles) were cut from each fish and moisture content were measured using a moisture balance which works by heating the tissues at 105 °C. Complete evaporation of water by spreading the tissues uniformly on the plate used in that balance. The percentage of the moisture content was recorded. Edible tissues (muscles) taken from different parts of the fish were dried in the thermolyne oven at 108 °C overnight using porcelain dishes. When sample was completely dried it was ground and kept in a well-sealed plastic containers to avoid capturing moisture from the atmosphere.

About 2 grams dried fish tissues from each weight of hamour fish were weighed in duplicate in Teflon containers for acid digestion. Acid digestion was carried out for three repeated times on the two different weights of hamour fish, following the same conditions and the average of fluoride content obtained was taken for both weights. 20 ml of concentrated nitric acid ($HNO_3$) was added to each Teflon container or vessel and stayed inside a fume cupboard for overnight for partial digestion. Vessels lids were opened or left released for the gradual releasing of $N_2O$ and other gases. Reagent blank was done simultaneously. The teflon vessels were capped uisng the capping/decapping station. Teflon vessels were placed in the teflon turn-table and put into the microwave oven for gradual digestion which called the wet ashing (acid

digestion). The digestion was conducted by adjusting the following microwave conditions and steps:

1. 10% power for 2 min.
2. 20% power for 2 min.
3. 20% power for 2 min.
4. 40% power for 3 min.

Releasing of excessive gases was needed between heating (digestion) processes. After the final step was conducted, turn-table with vessels was moved to the fume cupboard for gases and pressure releasing, then they were left until getting cold, followed by complete transferring of the digested samples solutions into 50 ml volumetric flasks by filtration through filter papers (Schleicher and Schüll) and completed to mark with deionized water. 80 gm of NaOH were weighed in volumetric flask of 500 ml and dissolved with deionized water and completed to mark. 10 ml of this alkali solution were used for the neutralization of 10 ml of the digested samples solutions with stirring. While measuring pH, more alkali solution was added dropwisely until solution's pH reach about 3. The solution's total volume was taken into account, then more neutralization using (15% Sod. Ac.) was diluted in the ratio of 9:1 acetate to sample till pH 5-6 is reached where the FISE is sensitive to detect fluoride ions.

**2.4.7 b. Checking electrode operation (slope) and calibration:**

Electrode operation or (slope) was checked by detecting 1 and 10 ppm fluoride/TISAB standard (Orion application standard solutions) and check the slope obtained, if within the applicable range, calibration

was done using 0.2 and 2 ppm fluoride standard solutions with 15% sod. Ac. in the ratio of 9:1 acetate to standard followed by equal volume of TISAB II.

**2.4.7 c. Sample analysis:**

The digested sample's solution which was already neutralized as mentioned before was analysed after adding of equal volume of TISAB II by measuring 3 volumes of the same sample using FISE, reading of meter was taken after stabilization and an average was taken. Readings were recorded for the blank and average was calculated. Fluoride ion concentration was calculated in $mgF^-/kg$ dry matter by the following equation:

$$\left(\overline{F^-} - \overline{BL}\right) \times DF_1 \times DF_2$$

Where $\overline{F^-}$ = Average fluoride readings.

$\overline{BL}$ = Average blank readings.

$D.F_1$ = Total volume of the digested sample's solution after neutralization with NaOH solution/volume taken of the digested sample solution.

$D.F_2$ =

$$\frac{\text{Total volume of the digested sample's solution before the neutralization with NaOH solution (50 mL)}}{\text{Weight of the dried sample (2 gm)}}$$

Cations were measured from the same prepared digested samples solutions before neutralization using ICP - ES (Egan, H., 1981) and their concentrations were calculated by the following equation: (blank was measured).

Cation conc. in mg/kg dry matter =

$$\frac{\text{(Reading-blank)} \times \text{Total volume (50 ml)}}{\text{Weight of sample (2 gm)}}$$

# RESULTS AND DISCUSSION

# CHAPTER III

# Part I

## Determination of Fluoride Ion in Some Drinking Water and Food Samples

## 3.1. Determination of Fluoride in water samples

### 3.1.1. Introduction:

Several years of extensive research shows conclusive evidence that fluoride is an essential element for human nutrition. The US Food and Nutrition Board of National Research Council has recently estimated adequate and safe daily intake of fluoride by individuals according to their age groups (e.g., 0.1-0.5 mg for infants less than 6 months, 0.2-1.0 mg for infants between 6-12 months, 0.5-2.5 mg for children between 1 and 6 years, 1.5-2.5 mg for children 7 years and adulthood, and 1.5 to 4.0 mg for adults) (Safe Drinking Water Committee, 1980). Furthermore, WHO has set a guide line value of 1.5 ppm of fluoride in drinking water with the remark that local or climatic conditions may necessitate adaptations (WHO, 1993).

It is well known that there is some correlation between dental health and fluoride content in drinking water. Water containing fluoride up to an optional concentration 1.5 ppm reduces dental caries especially among children, while consumption of drinking water containing excessive fluoride can result in mottling of teeth and dental fluorosis.

The optimal level of fluoride concentration in drinking water applicable to any given country or community depends on several factors.

a) Ambient temperature, high consumption of fluoride due to more intake of water in hot climatic conditions may lead to higher incidence of dental fluorosis. Consequently, the optimal concentration of fluoride in drinking water for cold region can not be applied to hot region.

b) Food habits of the population, most of the food materials contain fluoride with varies concentration level, fish and tea are known to be abundant in fluoride. Thus a community are habitual rich fluoride food, feedstuff and water might be harmful rather than beneficial.

According to the mentioned above the trace determination of fluoride in drinking water, food, feedstuff is becoming increasingly important due to its implications for environmental health. Because we have different source of drinking water in UAE, the following results indicate a survey of fluoride level in some samples of bottled, underground and desalinated water which are used as a drinking water.

### 3.1.2. Fluoride Content in Mineral Bottled Water:

The fluoride concentration level in the most common types of mineral bottled water was checked using ion chromatographic technique (IC) and ionic analyzer equipped with fluoride ion selective electrode (FISE).

The most common anionic species present in the various types of drinking water are $Cl^-$, $NO_3^-$, $SO_4^{2-}$ and $PO_4^{2-}$. Therefore, a Dionex standard solution mixture containing different concentration of the above mentioned anionic species and $F^-$ were prepared. The Dionex containing $F^-$ solutions was subjected to IC analysis to emphasize the operational conditions for analysis of water samples. The chromatograms of Dionex containing $F^-$ solution are represented in Fig's 3.1-3.3. It was found that the retention time of $F^-$ is different from the retention time of the other species indicating that the determination of fluoride anion in the presence of the other anionic species is possible without interfering effect. Also, the

calculated degree of recovery of $F^-$ concentration in presence of these anionic species is in the range of 98-101% (n = 5).

Figures 3.4 to 3.9 show a representative IC chromatograms for some drinking mineral bottled water samples. The calculated $F^-$ concentration levels in the checked drinking water samples are listed in Table 3.1. As well, the various bottled water samples were subjected for full anionic and cationic analysis using IC and ICP, the results of analysis are listed in Tables 3.2 and 3.3.

Fluoride ion concentration in the various bottled water samples was also determined by FISE technique with no treatment. It is generally recognized in the literature that the ISE analysis of such sample involves no critical steps such as sample preparation or pretreatment or decomposition and that potentiometry can be applied directly as there are no uncontrolled interferences resulting from the composition of the sample.

The $F^-$ determination was checked using the low level TISAB and TISAB II to be tested for their efficiency in measurement of $F^-$ and elimination of interferences. It was found that TISAB II buffer was more effective where as using this buffer leads to fast response and highly degree of recovery. It is well known that the use of TISAB II buffer solution prevents the complexation and interfering effect of metal cation such as Al(III) and Fe(III) in the $F^-$ determination using ISE. By using the optimum buffer (TISAB II), the FISE technique was applied to analysis of $F^-$ concentration level in the some of the commonly used drinking bottled water (Table 3.1).

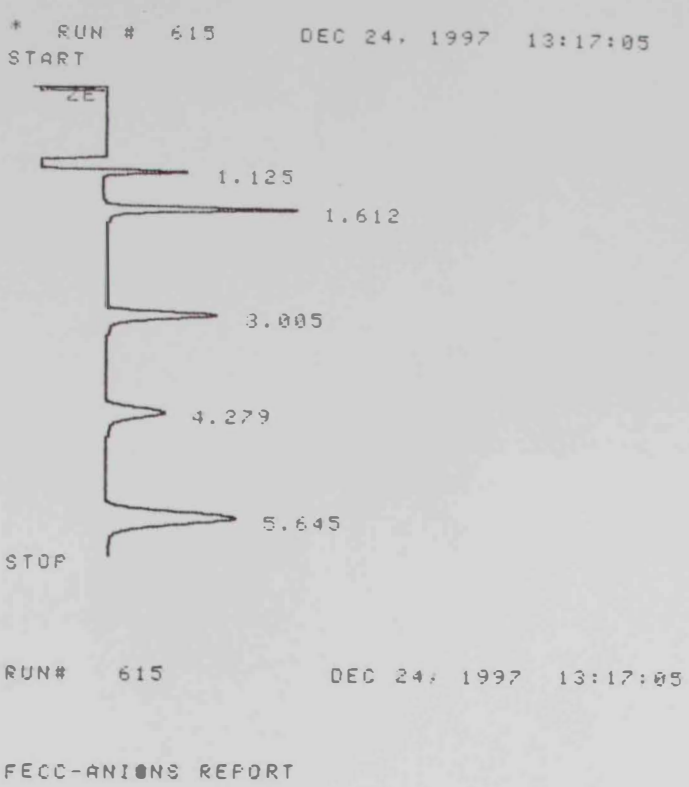



Fig. 3.1. One-point calibration chromatogram for Dionex standard solution mixture containing $F^-$ (0.2 ppm), $Cl^-$ (0.3 ppm), $NO_3^-$ (1.0 ppm), $PO_4^{3-}$ (1.5 ppm) and $SO_4^{2-}$ (1.5 ppm).

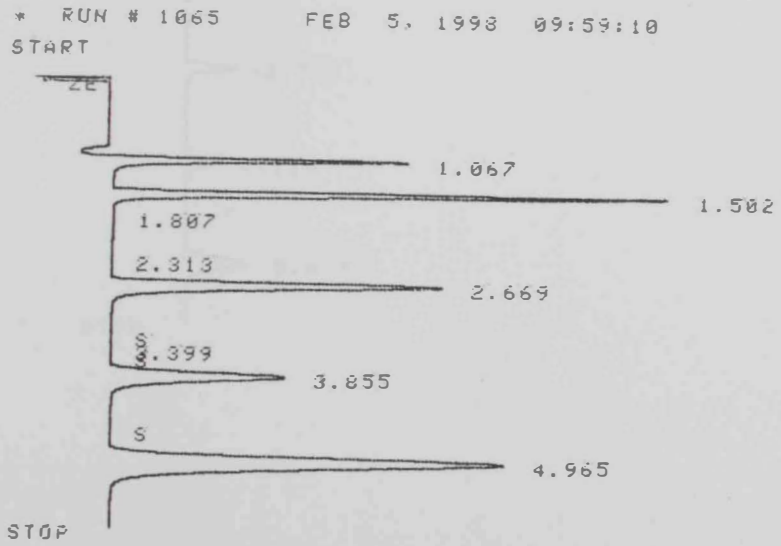



Fig. 3.2. One-point calibration chromatogram for Dionex standard solution mixture containing $F^-$ (2 ppm), $Cl^-$ (3 ppm), $NO_3^-$ (10 ppm), $PO_4^{3-}$ (15 ppm) and $SO_4^{2-}$ (15 ppm).

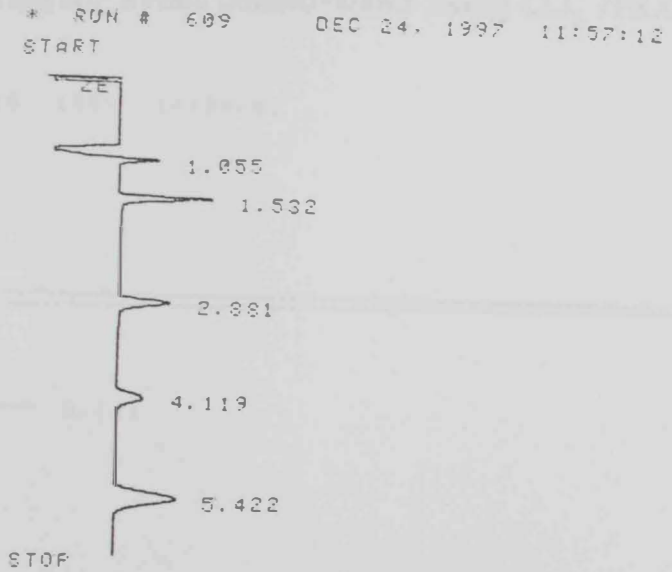



Fig. 3.3. Two-point calibration chromatogram for Dionex standard solution mixture containing $F^-$ (0.2, 2 ppm), $Cl^-$ (0.3, 3 ppm), $NO_3^-$ (1.0, 10 ppm), $PO_4^{3-}$ (1.5, 15 ppm) and $SO_4^{2-}$ (1.5, 15 ppm).

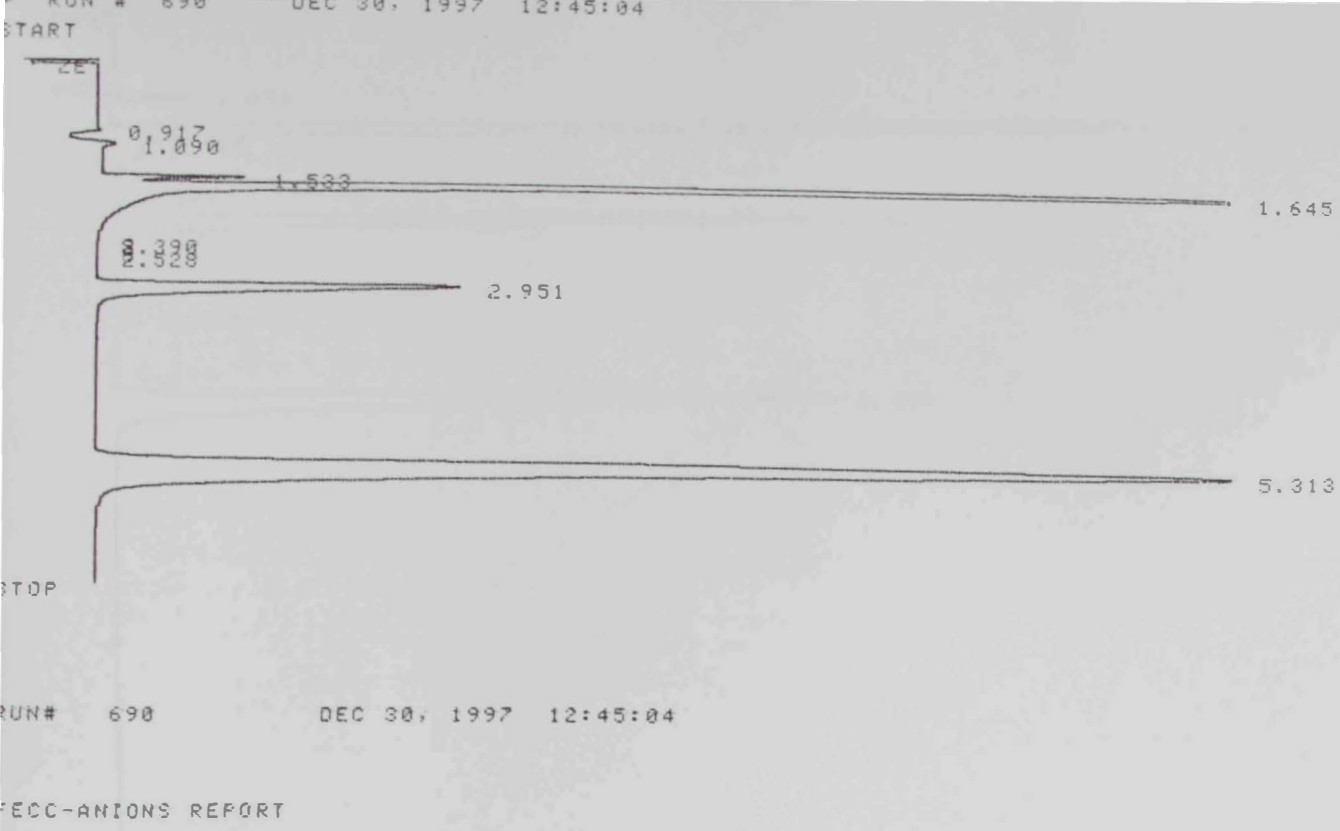



Fig. 3.4. Chromatogram for Evian bottled-water using $CO_3^{2-}/HCO_3^-$ eluent solution.

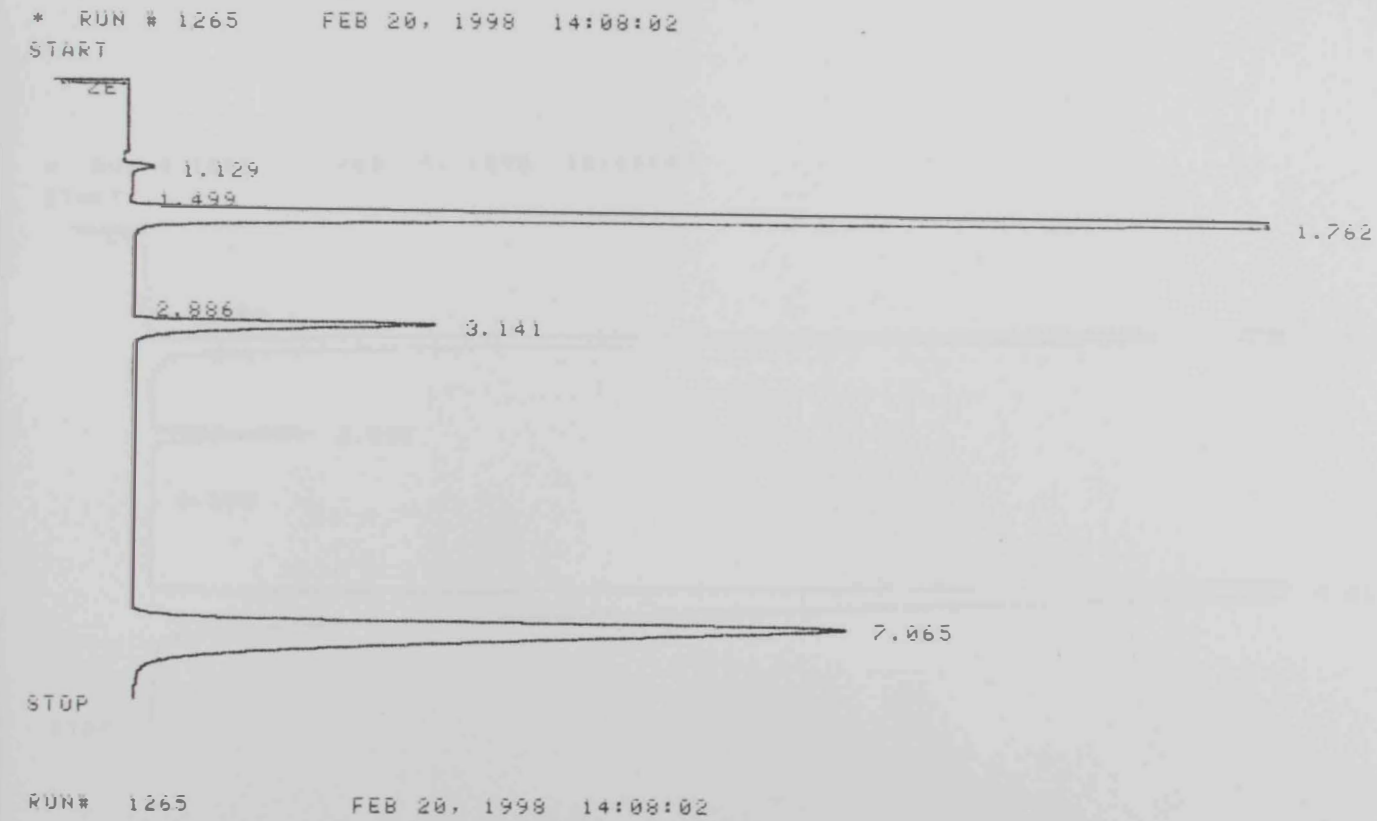



Fig. 3.5. Chromatogram for Tanuf bottled-water using $CO_3^{2-}/HCO_3^-$ eluent solution.

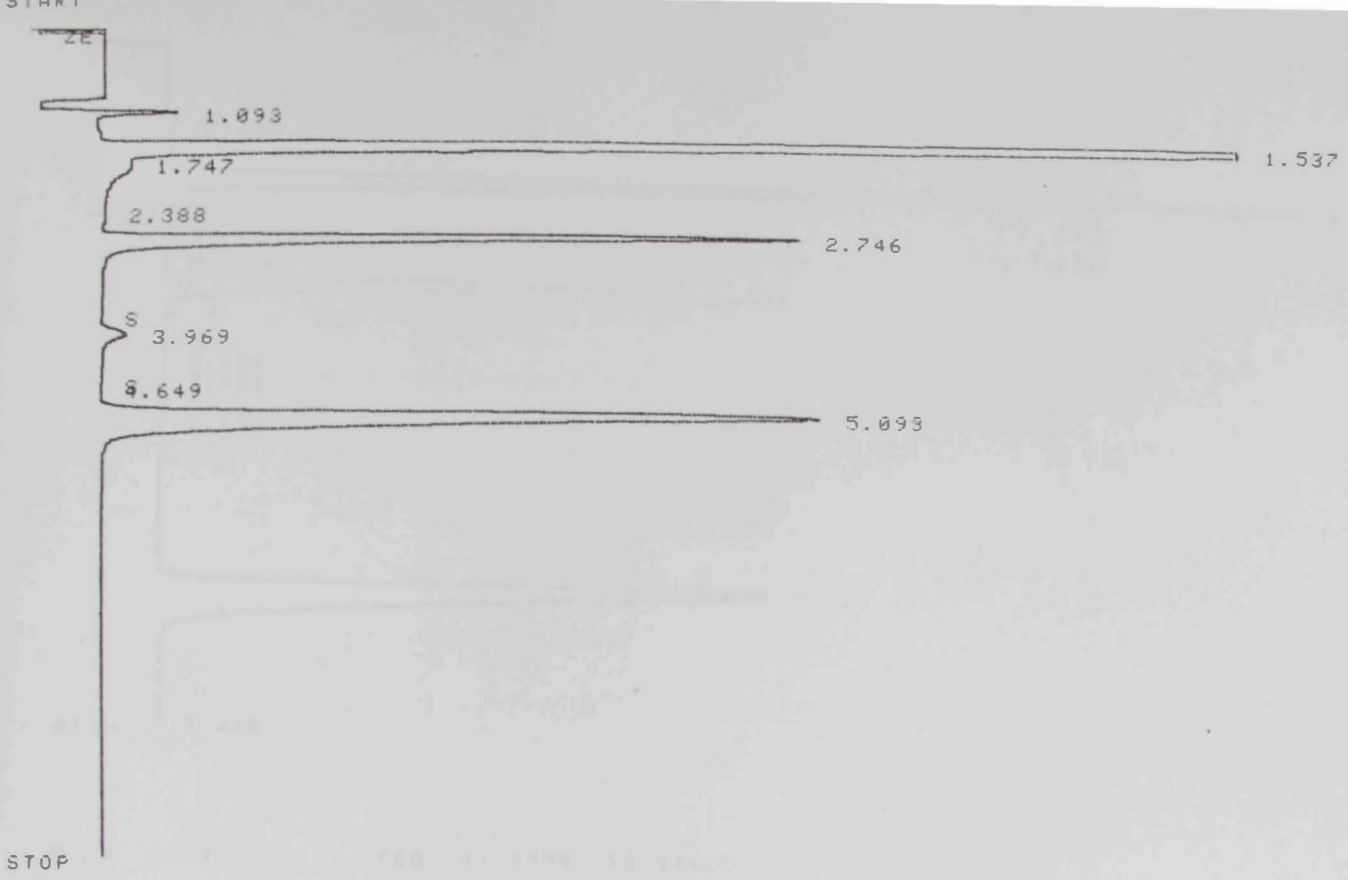



Fig. 3.6. Chromatogram for Volvic bottled-water using $CO_3^{2-}/HCO_3^-$ eluent solution.

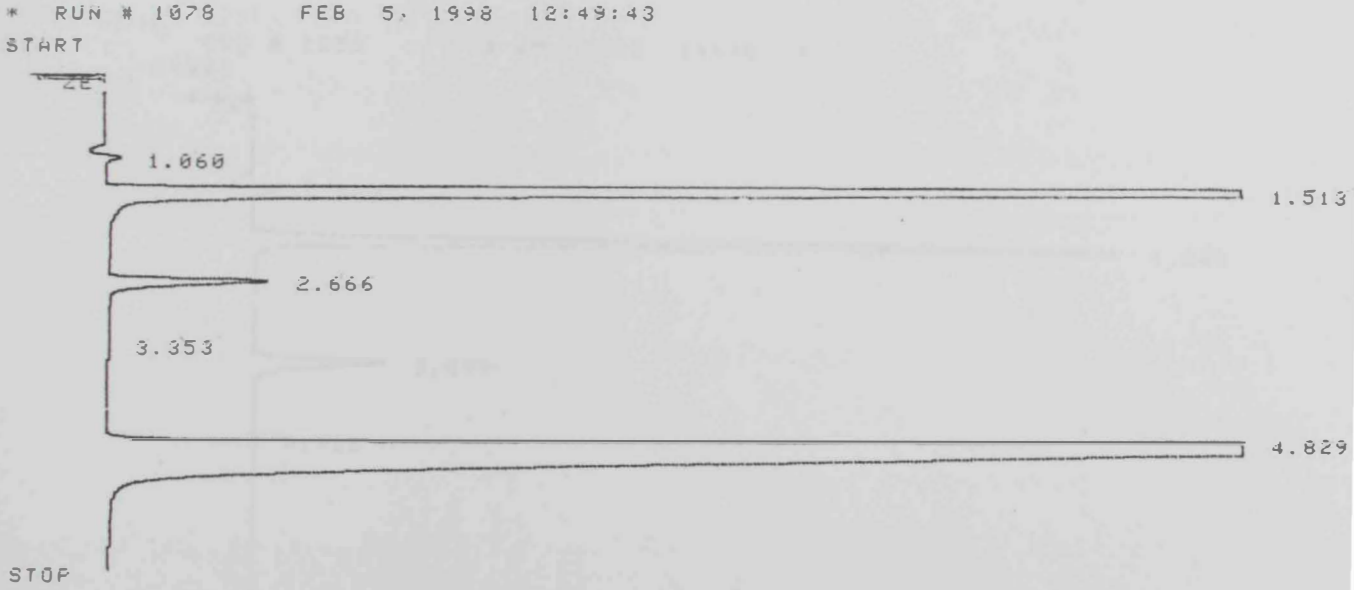



Fig. 3.7. Chromatogram for Aqua Idka bottled-water using $CO_3^{2-}/HCO_3^-$ eluent solution.

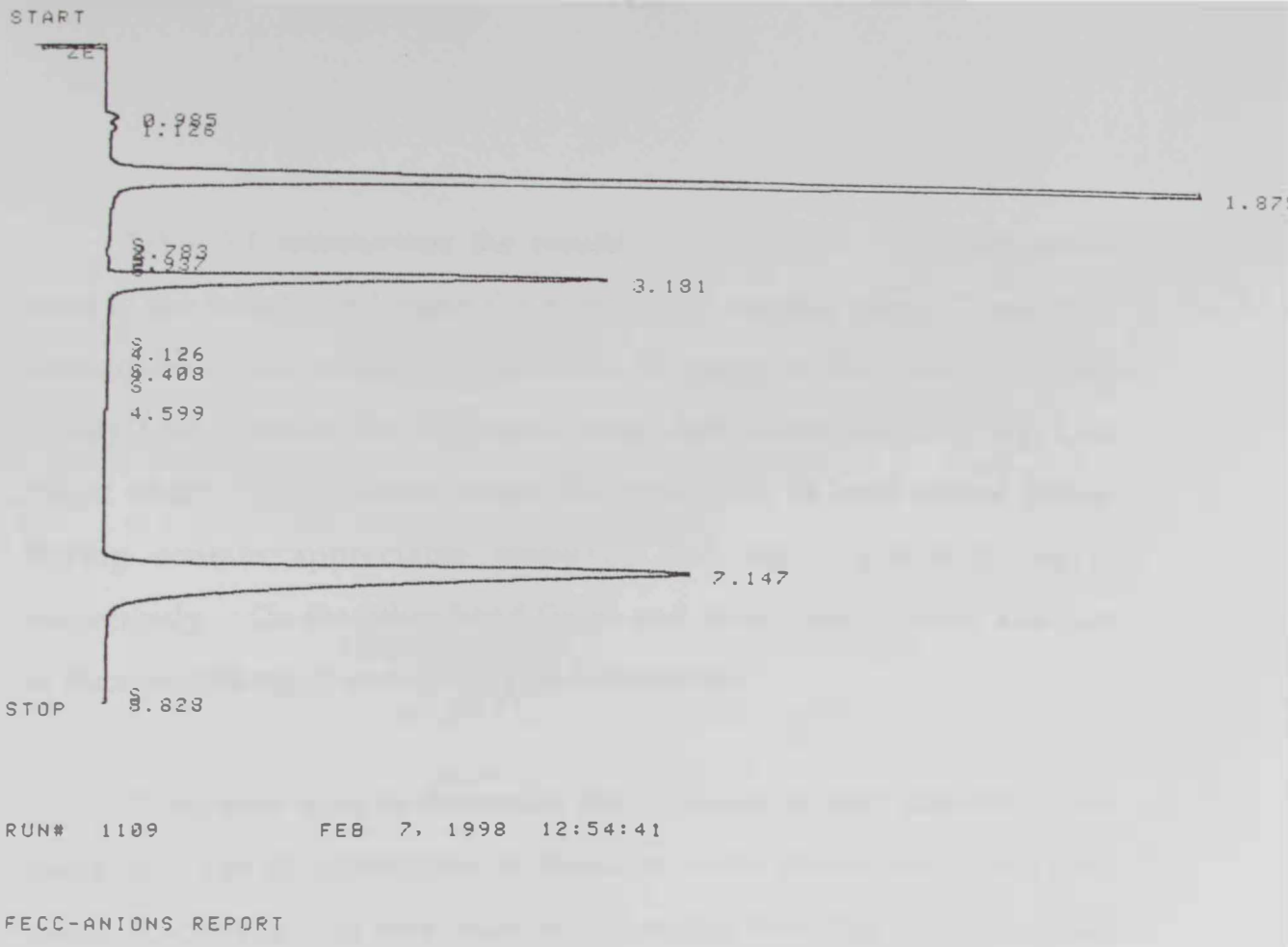



Fig. 3.8. Chromatogram for Perrier bottled-water using $CO_3^{2-}/HCO_3^-$ eluent solution.

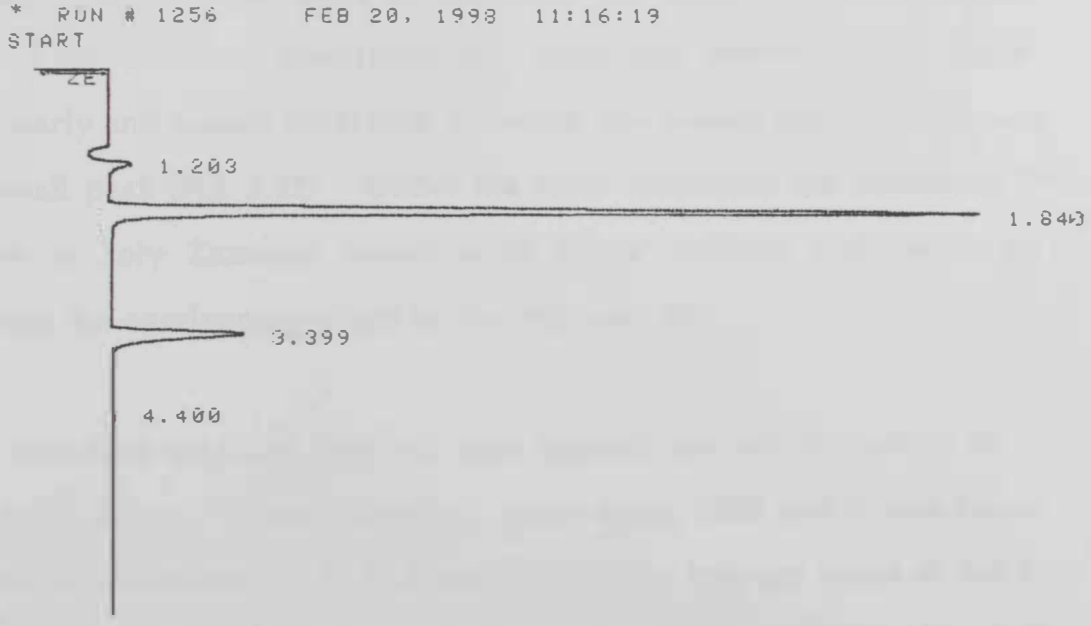



Fig. 3.9. Chromatogram for Falcon Spring bottled-water using $CO_3^{2-}/HCO_3^-$ eluent solution.

Table 3.1 summarizes the results of analysis of $F^-$ concentration level in the investigated mineral bottled water samples using IC and FISE techniques. The fluoride content is in the range of N.D. value in some locally bottled water like Emirates, Jeema and Masafi and 0.35 mg/L in Tanuf water. Some bottled water like Evian and of local source Falcon Spring contain appreciable amounts, 0.16 mg/L and 0.32 mg/L, respectively. On the other hand Gulfa and Al-Ain contain low amounts of fluoride 0.06 mg/L and 0.05 mg/L, respectively.

Trials were done to determine the $F^-$ content in holy Zamzam water using IC. The chromatogram of Zamzam water shows two overlapped peaks at retention time very close to $F^-$ retention time (Fig. 3.10). It should be mentioned that spike of Zamzam water with 1.0 ppm $F^-$ (Fig. 3.11) confirms that the peak with longest retention time is $F^-$ peak. Dilution of Zamzam water sample leads to minimize the effect of the overlapped peaks of the unknown interfered ion. Four fold dilution shows the $F^-$ peak clearly and almost separated, however, the second peak appears as a very small peak (Fig. 3.12). Under the latter conditions the calculated $F^-$ content in holy Zamzam water using IC is unlikely and very high reflecting the overlapping effect of the unknown ion.

Standard addition method was applied for determination of $F^-$ concentration level in holy Zamzam water using FISE and it was found that the concentration of $F^-$ is 0.398 mg/L. The average value of the $F^-$ content in the 15 samples under investigation of the drinking water is

$0.103 \pm 0.063$ mg/L. It can be concluded that the mineral bottled water sold in UAE market is not a good source for fluoride ion.

The samples under investigation were subjected to other anion analysis e.g. chloride, nitrate, phosphate and sulphate (Table 3.2). The purpose of such analysis is to see if there is any correlation between the fluoride content in bottled water and these anions. All samples contained chloride in the range of 41.97 mg/L as a maximum in Gulfa water and 2.9155 mg/L in High land spring as the minimum and the average content is 21.43 mg/L. The range of nitrate content is between 11.098 mg/L in Masafi water as the highest and 0.57 mg/L in High land spring as lowest. The sulphate ($SO_4^{-2}$) content ranges between 68.38 mg/L in Aqua Idka as maximum and 5.73 mg/L in Oasis as the minimum and the average value of $SO_4^{2-}$ content is 21.598 mg/L. However, it is found that there is no correlation between various anions content and fluoride content in the studied bottled water samples. The $PO_4^{3-}$ was not detected in the investigated samples except in Volvic (0.724 mg/L) and Falcon spring (0.900 mg/L $PO_4^{3-}$).

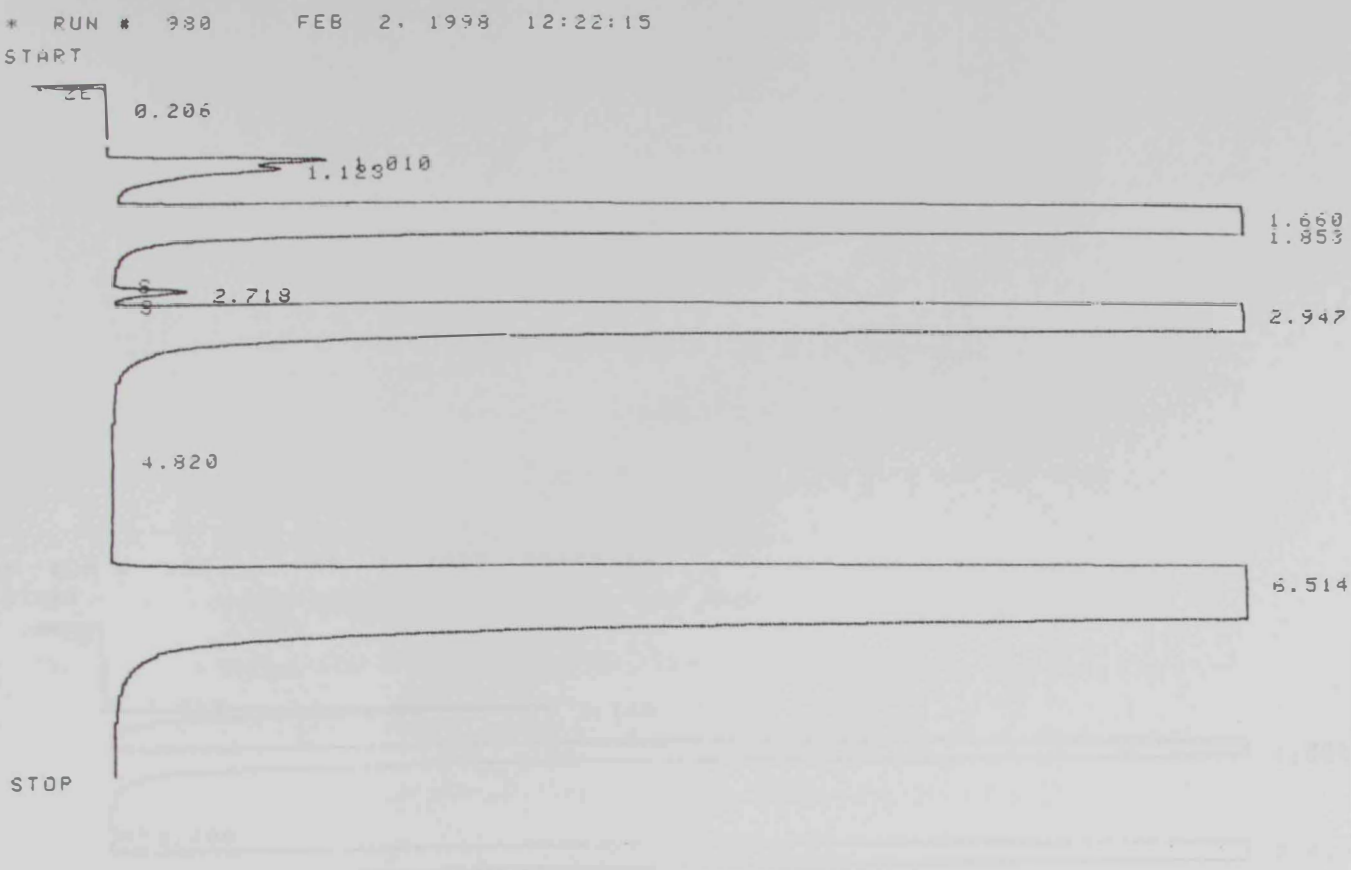



Fig. 3.10. Chromatogram for holy Zamzam water using $CO_3^{2-}/HCO_3^-$ eluent solution.

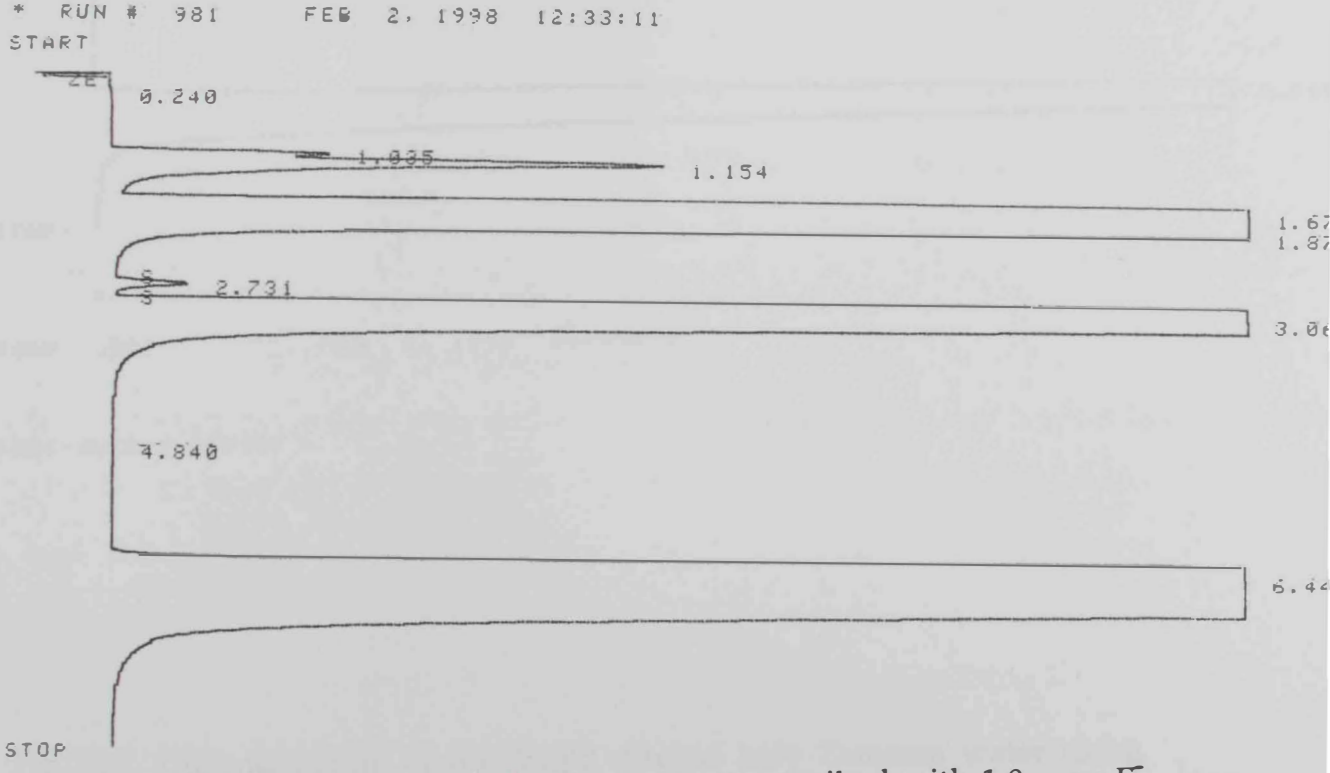



Fig. 3.11. Chromatogram for holy Zamzam water spiked with 1.0 ppm $F^-$ using $CO_3^{2-}/HCO_3^-$ eluent solution.

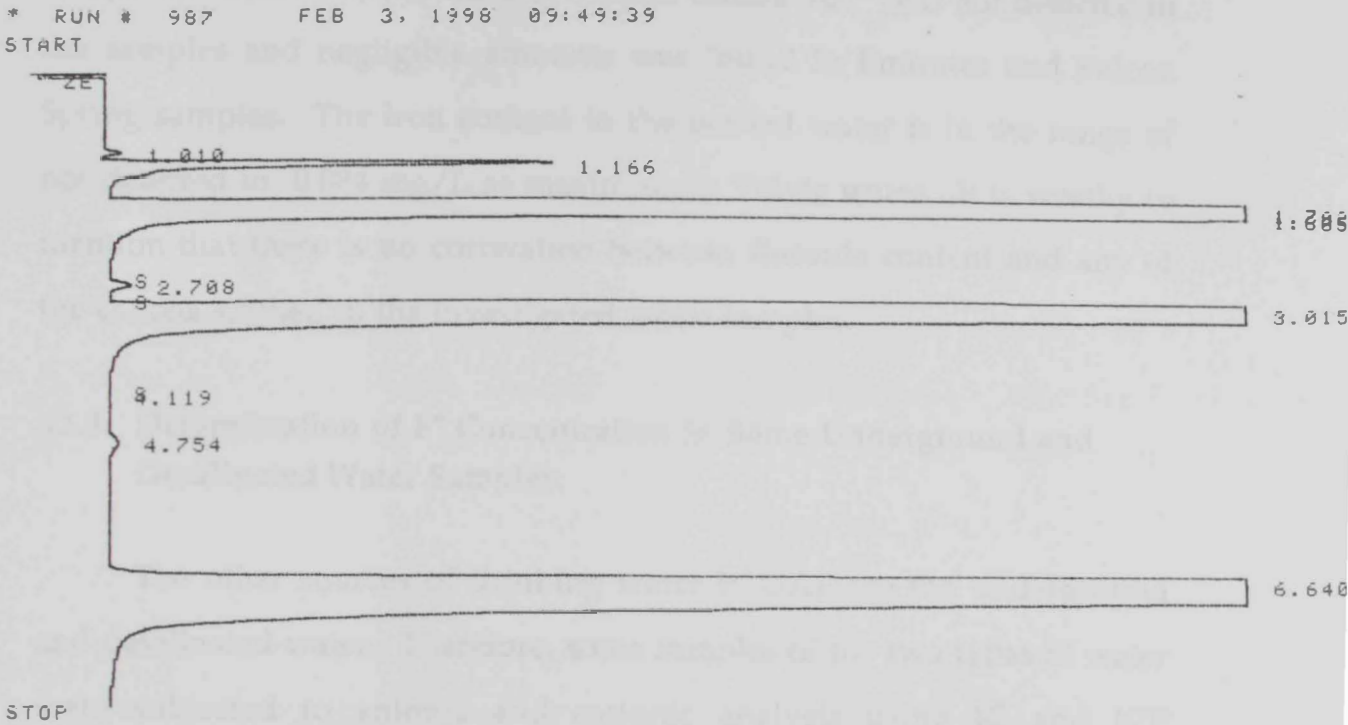



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Fig. 3.12. Chromatogram of the 4-fold diluted holy Zamzam water using $CO_3^{2-}/HCO_3^-$ eluent.

The cations $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$ and $Al^{3+}$ were analyzed in the 15 samples of bottled water, the results are listed in Table 3.3., holy Zamzam water contains high amounts of sodium (189.60 mg/L), potassium (84.96 mg/L), calcium (154.32 mg/L) and magnesium (45.05 mg/L). Holy Zamzam water is a special type of water and we can not compare it with the other mineral bottled waters. $Al^{3+}$ was not detected in the samples and negligible amounts was found in Emirates and Falcon Spring samples. The iron content in the bottled water is in the range of not detected to 0.084 mg/L as maximum in Volvic water. It is worthy to mention that there is no correlation between fluoride content and any of the cations studied in the investigated water samples.

### 3.1.3. Determination of $F^-$ Concentration in Some Underground and Desalinated Water Samples:

The other sources of drinking water in UAE are the underground and desalinated water. Therefore, some samples of the two types of water were subjected to anionic and cationic analysis using IC and ICP techniques (Tables 3.4, 3.5). The $F^-$ concentration level in the sample under investigation was determined using IC (Table 3.4). The samples of the underground water were collected from Liwa, the western region of Abu Dhabi area and it was found that these samples contain remarkable high concentration level of $F^-$ (1.5-5.7 mg/L). It can be concluded that drinking of such water type is unacceptable because it may lead to mottling of teeth and dental fluorosis for the children as well as skeletal fluorosis as noticed from the urine samples which were brought to the Food and

Environment Control Centre for fluoride analysis of some patients who have skeletal fluorosis and were admitted in Al-Jazeera hospital.

The underground water samples were collected from 5 wells at Liwa, Abu-Dhabi. The samples were subjected to full anionic and cationic analysis (Tables 3.4, 3.5) before and after filtration. The filtration was carried out to remove parts of high salts content. Fig's 3.13-3.19 show that histograms distribution of $F^-$ and the various anions in the water samples collected from the 5 wells under investigation before and after filtration.

As we expect, the results of analysis of the desalinated water samples indicate that the fluoride ion was not detected, whereas it contains relatively lower concentration level of $NO_3^-$, $SO_4^{2-}$ and some metal cations (Tables 3.6, 3.7). It is worthly to mention that according to the WHO guideline value of 1.5 ppm of $F^-$ in drinking water the using of desalinated water as a main source of drinking water is not healthy and may lead to dental caries especially among the children.

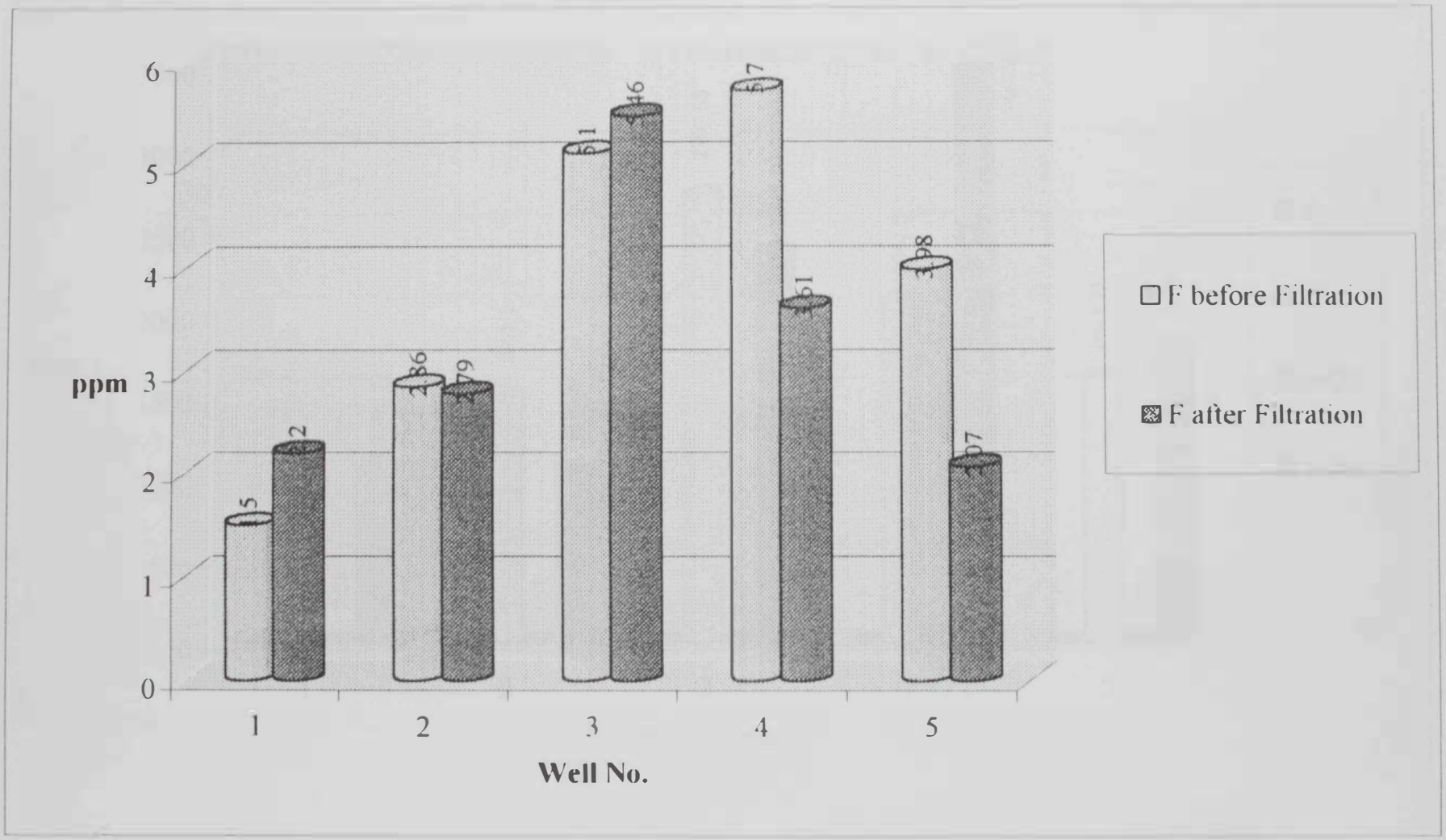


**Fig. 3.13 Concentration level of F⁻ before and after filtration in different wells (underground water sources).**

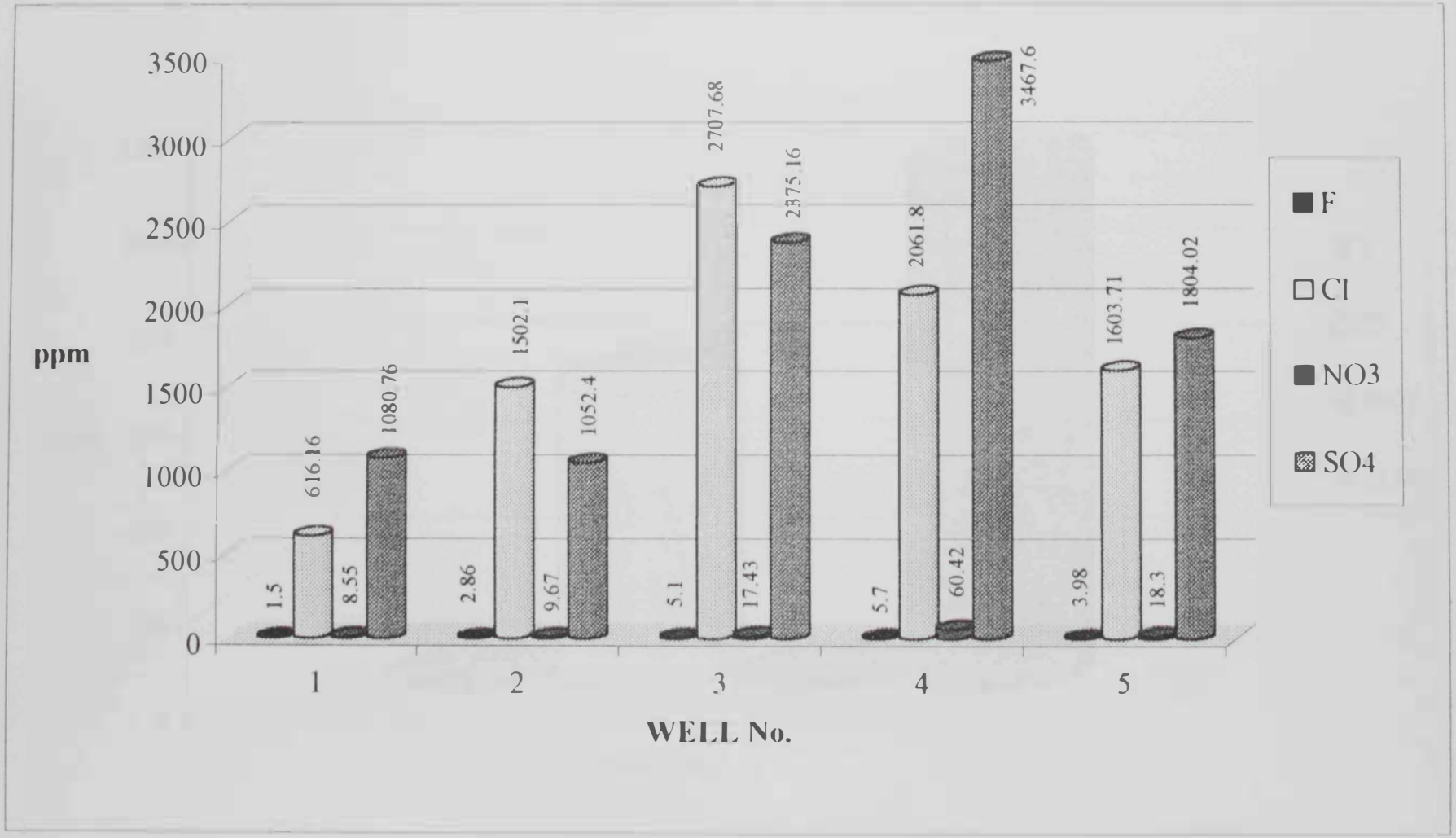


**Fig . 3.14 Concentration level of $F^-$, $Cl^-$, $NO3^-$ and $SO4^{-2}$ in the different wells (underground water sources)**

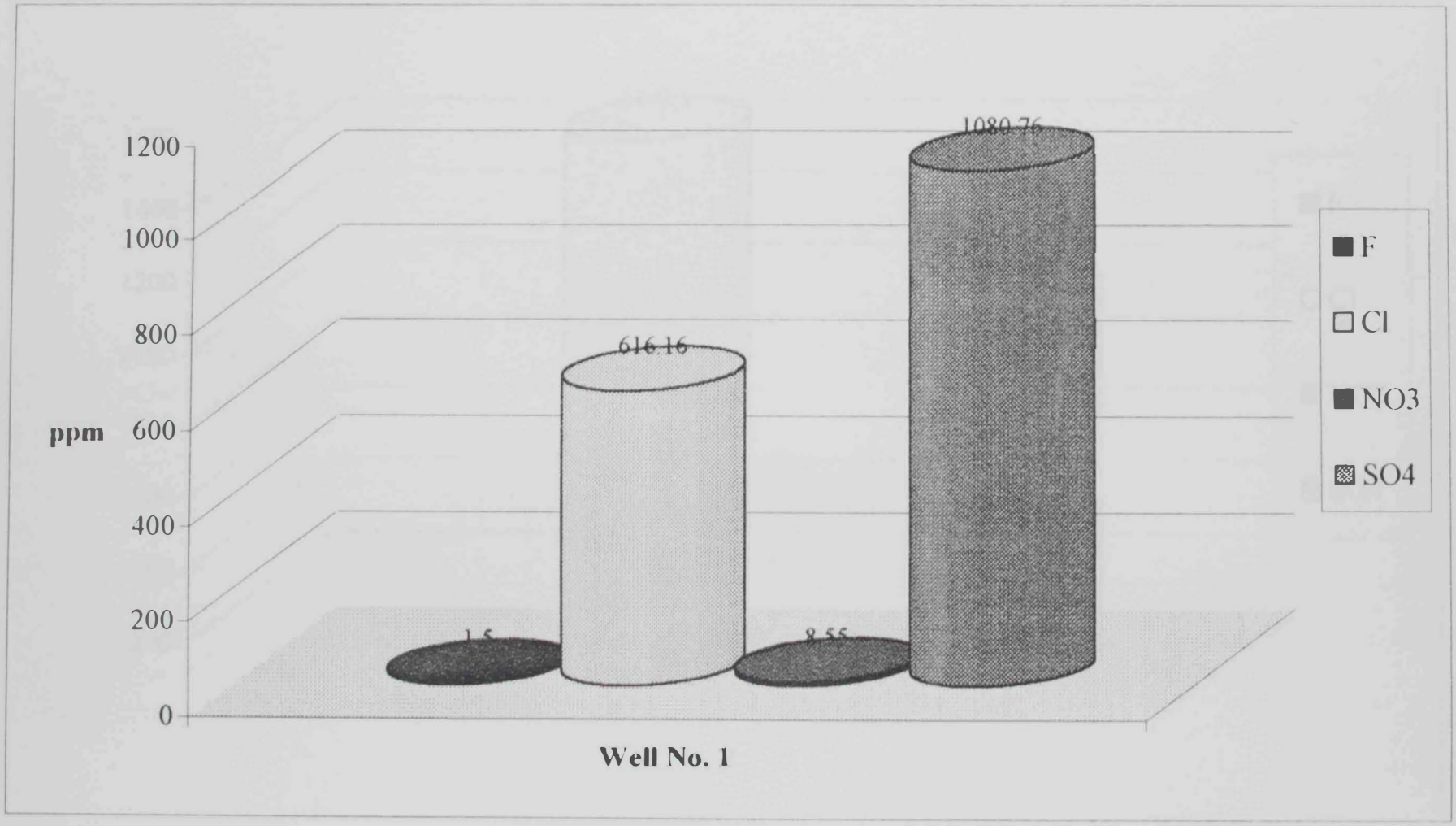


**Fig .3.15. Concentration level of $F^-$, $Cl^-$, $NO3^-$ and $SO4^{-2}$ in well No. 1 (underground water source)**

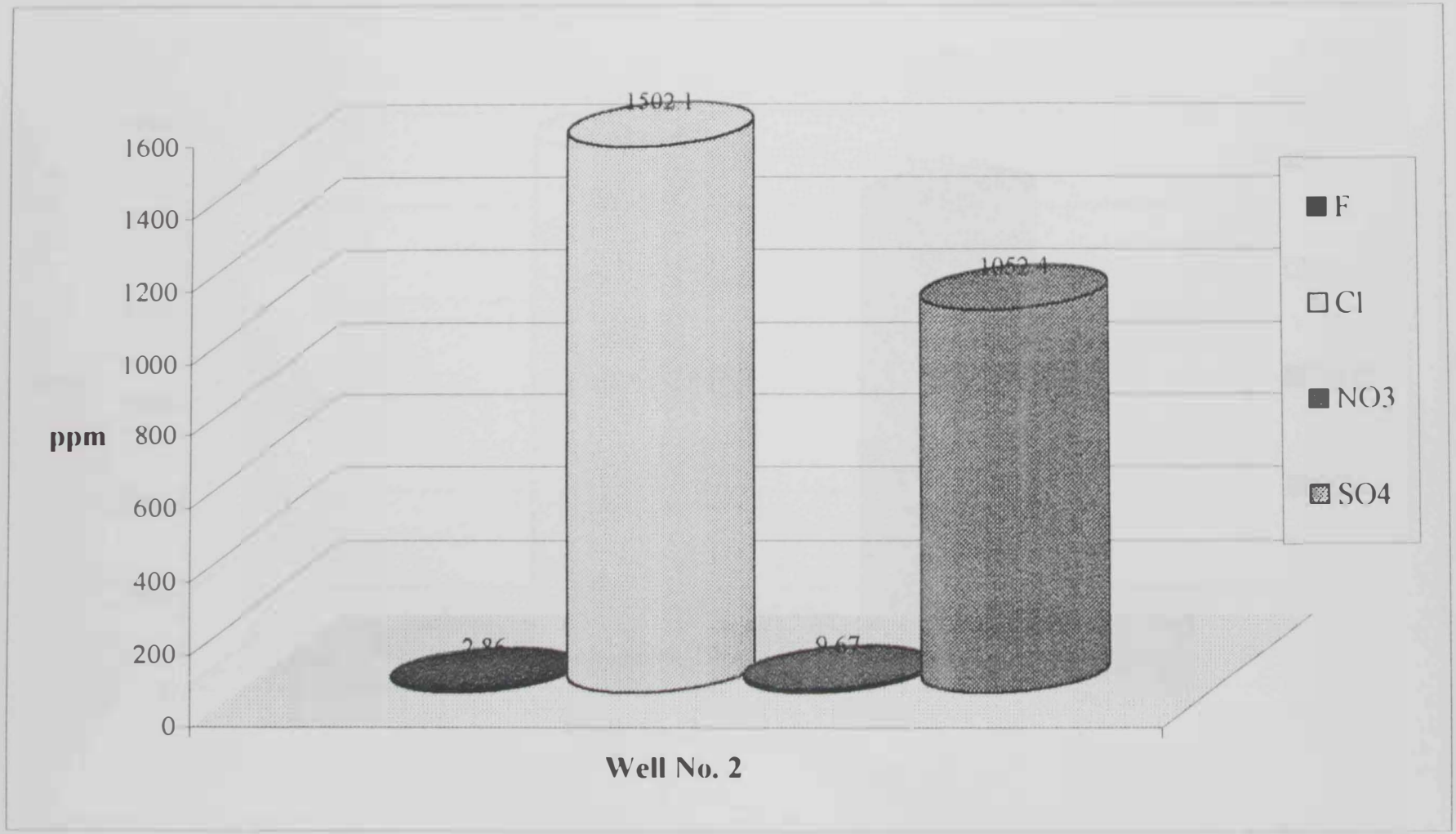


**Fig .3.16 Concentration level of $F^-$, $Cl^-$, $NO3^-$ and $SO4^{-2}$ in well No. 2 (underground water source)**

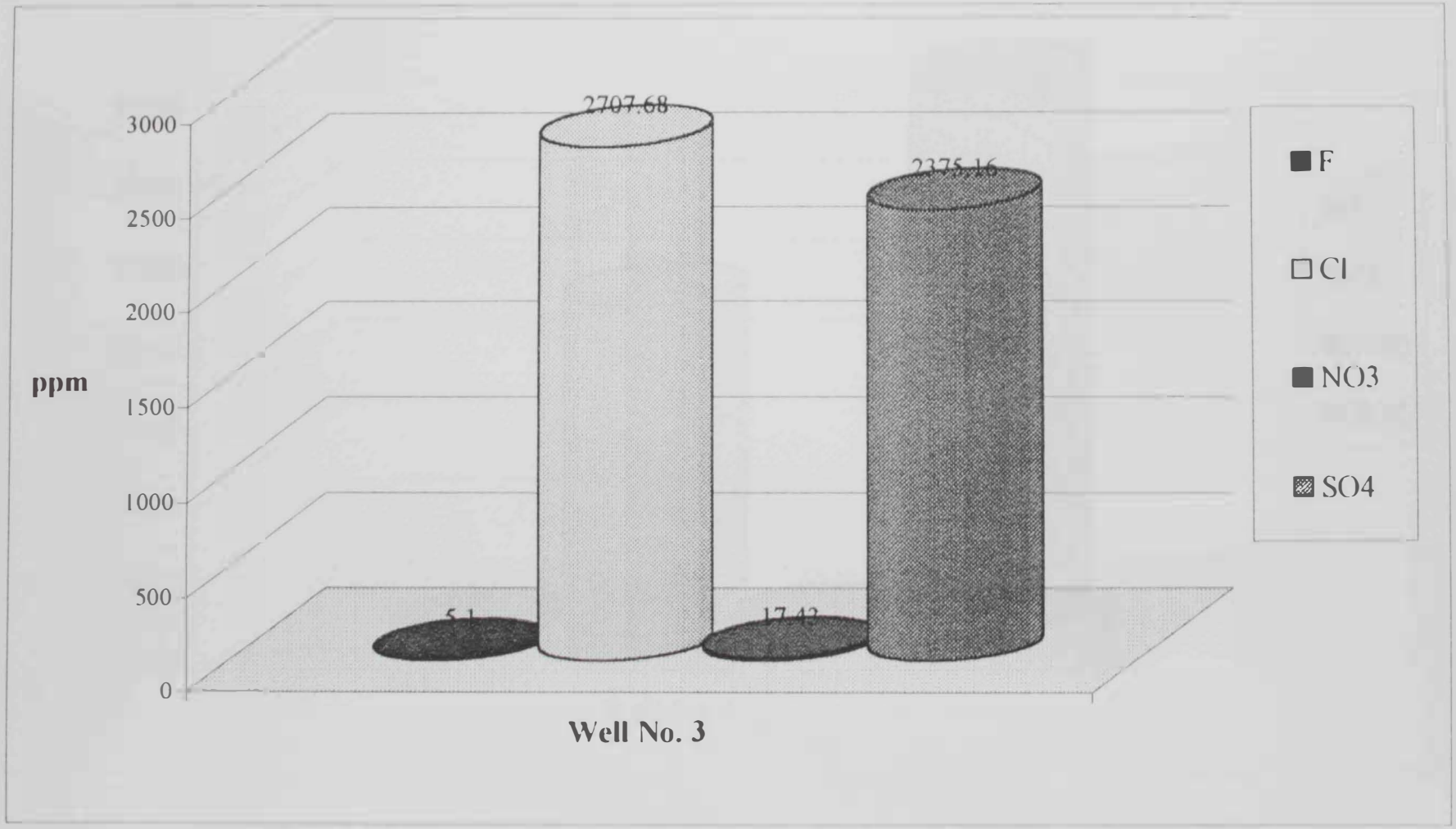


**Fig. 3.17 Concentration level of $F^-$, $Cl^-$, $NO3^-$ and $SO4^{-2}$ in well No. 3 (underground water source)**

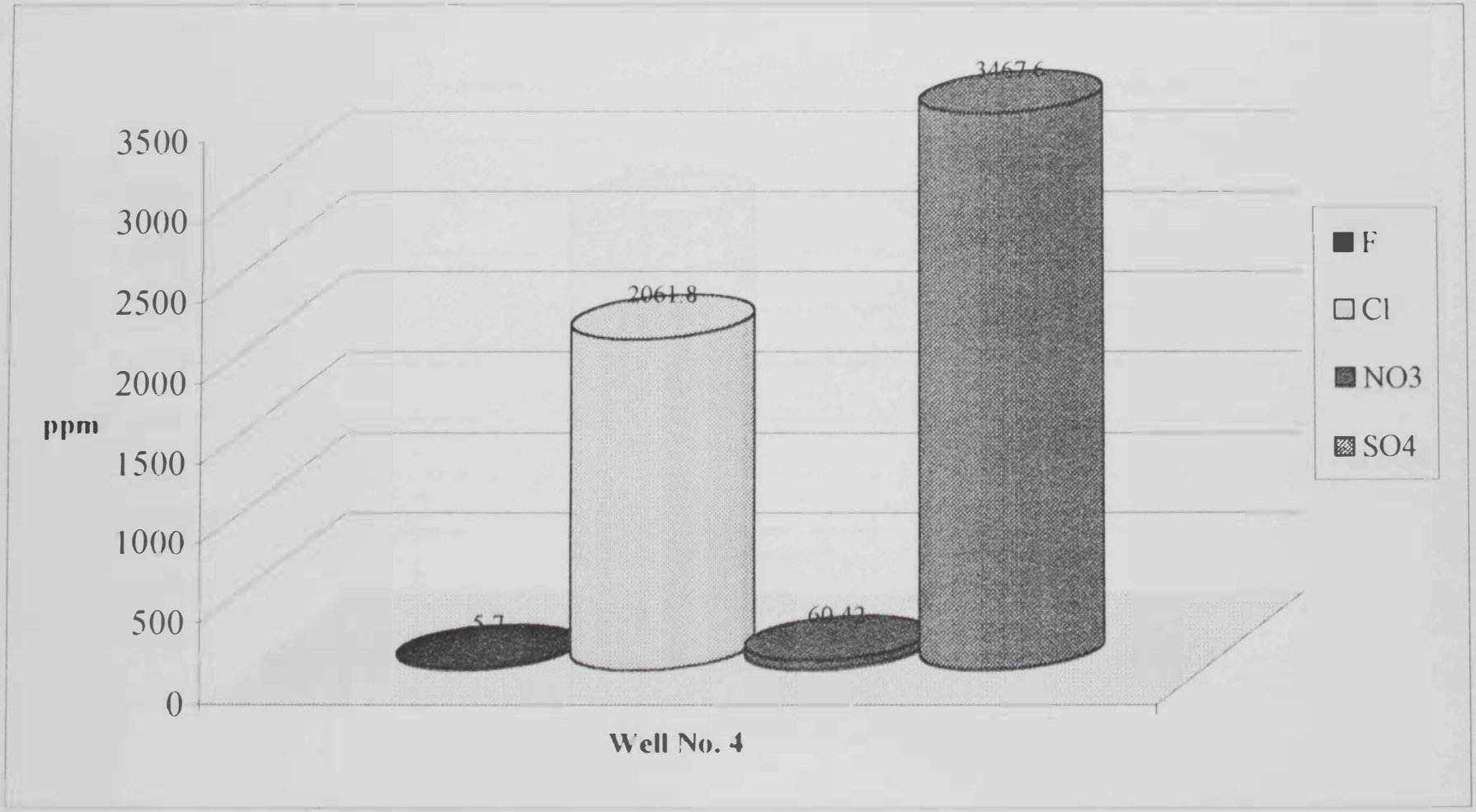


**Fig . 3.18 Concentration level of $F^-$, $Cl^-$, $NO3^-$ and $SO4^{-2}$ in well No. 4 (underground water source)**

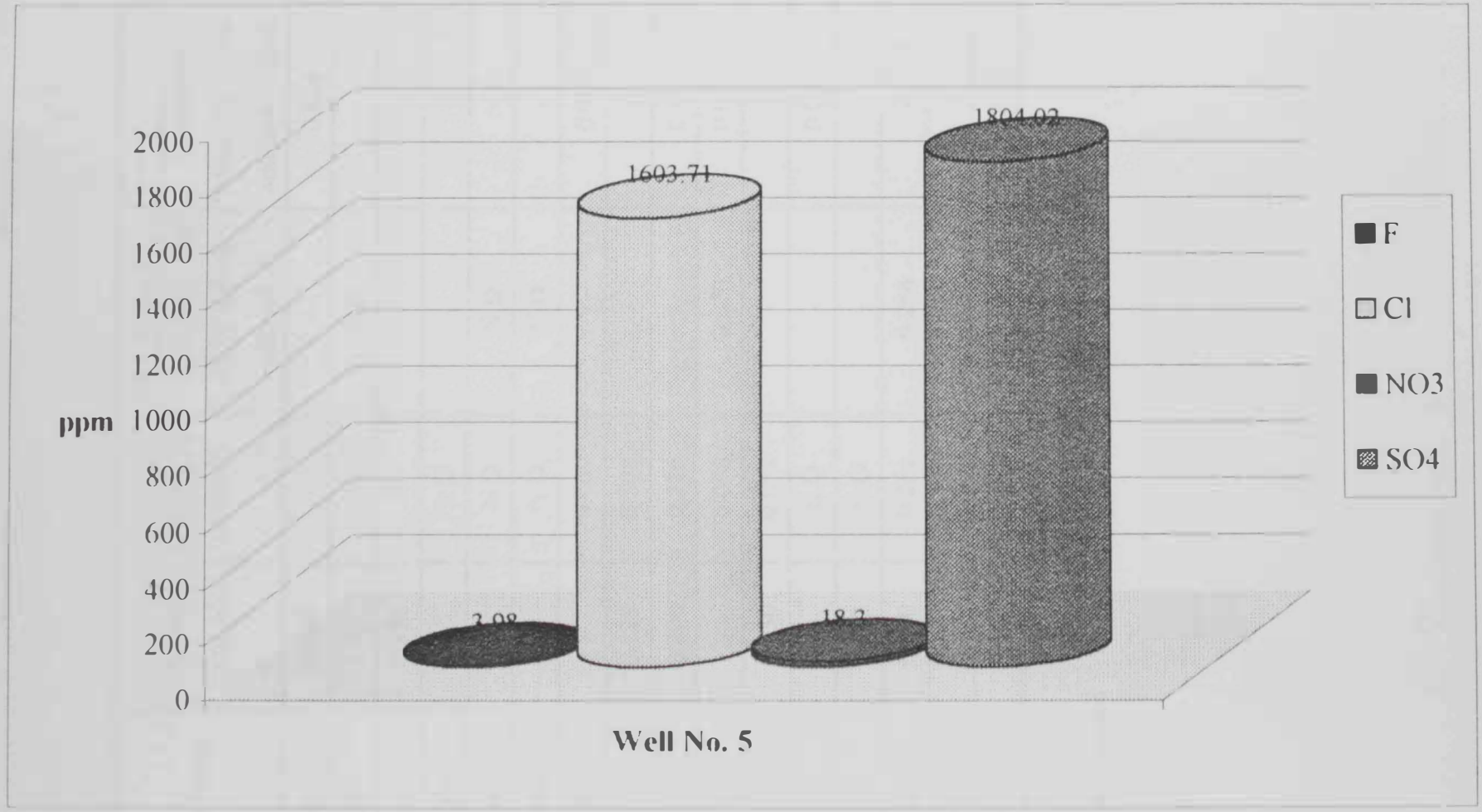


**Fig .3.19 Concentration level of $F^-$, $Cl^-$, $NO3^-$ and $SO4^{-2}$ in well No. 5 (underground water source)**

**Table( 3.1).Results of $F^-$ analysis in the different types of bottled mineral water .**

| No. | Bottled Water | $F^-$ Conc. in mg /L | | | |
|---|---|---|---|---|---|
| | | Determined using ISE | Determined using IC | Determined using IC by spiking with std. $F^-$ | Determined using ISE by std. addition method. |
| 1 | Evian | 0.162 | - | - | 0.128 |
| 2 | Awafi | - | N.D | N.D | - |
| 3 | Tanuf | 0.352 | - | - | - |
| 4 | Emirates | - | N.D | - | - |
| 5 | Oasis | - | N.D | N.D | - |
| 6 | Geema | - | N.D | N.D | - |
| 7 | Gulfa | - | 0.060 | - | 0.081 |
| 8 | Volvic | 0.229 | 0.202 | - | - |
| 9 | Aqua Idka | 0.206 | 0.216 | - | 0.186 |
| 10 | Perrier | - | 0.070 | 0.070 | 0.051 |
| 11 | High Land Spring | 0.050 | 0.079 | - | - |
| 12 | Masafi | - | N.D | - | 0.055 |
| 13 | Alain | 0.052 | N.D | - | - |
| 14 | Falcon Spring | 0.300 | 0.261 | 0.288 | - |
| 15 | Super Gulf | - | N.D | - | - |
| 16 | Zamzam | 0.364 | - | - | 0.398 |

N.D. = Not Detected

**Table ( 3.2 ). Results of anion analysis in the different types of bottled mineral water using IC .**

| No. | Bottled Water | Source | Conc. mg /L | | | |
|---|---|---|---|---|---|---|
| | | | $Cl^-$ | $NO3^-$ | $PO4^{-3}$ | $SO4^{-2}$ |
| 1 | Evian | France | 4.740 | 3.191 | N.D. | 11.552 |
| 2 | Awafi | Ras Al Khaima | 5.887 | 4.521 | N.D. | 6.037 |
| 3 | Tanuf | Oman | 14.250 | 9.368 | N.D. | 41.199 |
| 4 | Emirates | Al Fujaira | 35.425 | 8.292 | N.D. | 39.410 |
| 5 | Oasis | Abu Dhabi | 25.850 | 2.542 | N.D. | 5.727 |
| 6 | Geema | Ajman | 19.760 | N.D. | N.D. | N.D. |
| 7 | Gulfa | Ajman | 41.975 | 6.540 | N.D. | 45.768 |
| 8 | Volvic | France | 5.696 | 5.128 | 0.724 | 6.619 |
| 9 | Aqua Idka | Silovakia | 41.550 | 6.208 | N.D. | 68.380 |
| 10 | Perrier | France | 19.505 | 15.617 | N.D. | 37.665 |
| 11 | High Land Spring | Scotland | 2.916 | 0.573 | N.D. | 7.163 |
| 12 | Masafi | Ras Al Khaima | 37.960 | 11.098 | N.D. | 15.207 |
| 13 | Al Ain | Al Ain | 29.950 | 6.821 | N.D. | 12.879 |
| 14 | Falcon Spring | Dubai | 5.514 | 4.267 | 0.900 | 6.487 |
| 15 | Super Gulf | Om Al Quain | 30.510 | 7.167 | N.D. | 19.880 |
| 16 | Zamzam | Mekka | 182.950 | 156.450 | N.D. | 154.900 |

**Table ( 3.3 ) Results of cation analysis in the different types of bottled mineral water using ICP.**

| No. | Bottled Water | Conc. mg /L | | | | | |
|---|---|---|---|---|---|---|---|
| | | $Na^{+}$ | $K^{+}$ | $Ca^{+2}$ | $Mg^{+2}$ | Total Fe | $Al^{+3}$ |
| 1 | Evian | 5.350 | 1.940 | 79.430 | 31.490 | 0.013 | N.D |
| 2 | Awafi | 21.080 | 3.540 | 1.150 | 0.230 | N.D | N.D |
| 3 | Tanuf | 23.050 | 4.320 | 37.000 | 28.970 | N.D | N.D |
| 4 | Emirates | 28.470 | 3.930 | 3.710 | 46.160 | N.D | 0.010 |
| 5 | Oasis | 29.610 | 1.670 | 7.310 | 3.590 | N.D | N.D |
| 6 | Geema | 30.030 | 4.980 | 8.410 | N.D | N.D | N.D |
| 7 | Gulfa | 16.850 | 1.540 | 16.580 | 47.550 | N.D | N.D |
| 8 | Volvic | 9.590 | 5.520 | 10.230 | 9.047 | 0.084 | N.D |
| 9 | Aqua Idka | 2.780 | 1.020 | 53.920 | 14.150 | 0.058 | N.D |
| 10 | Perrier | 8.000 | 0.780 | 104.720 | 2.680 | N.D | N.D |
| 11 | High Land Spring | 4.390 | 1.020 | 34.050 | 12.480 | 0.061 | N.D |
| 12 | Masafi | 14.840 | 1.520 | 4.150 | 24.280 | 0.030 | N.D |
| 13 | Alain | 12.640 | 0.830 | 5.670 | 14.170 | 0.050 | N.D |
| 14 | Falcon Spring | 11.480 | 11.610 | 12.910 | 10.240 | N.D | 0.040 |
| 15 | Super Gulf | 23.660 | 3.040 | 9.220 | 28.640 | N.D | N.D |
| 16 | Zamzam | 189.590 | 84.960 | 154.320 | 45.050 | N.D | N.D |

**Table ( 3.4 ) Results of anion analysis in the underground water sources in LIWA in mg/L before and after filtration using IC.**

| well no. | Location | Before Filtration | | | | |
|---|---|---|---|---|---|---|
| | | $F^-$ | $Cl^-$ | $NO_3^-$ | $PO_4^{-3}$ | $SO_4^{-2}$ |
| 1 | Al NASASHA | 1.500 | 616.160 | 8.550 | N.D | 1080.760 |
| 2 | Al JEERA | 2.860 | 1502.100 | 9.670 | N.D | 1052.400 |
| 3 | AL JEPANA | 5.100 | 2707.680 | 17.430 | N.D | 2375.160 |
| 4 | Al Nafeer | 5.700 | 2061.800 | 60.420 | N.D | 3467.600 |
| 5 | AL OWANAN | 3.980 | 1603.710 | 18.300 | N.D | 1804.020 |

| well no. | Location | After Filtration | | | | |
|---|---|---|---|---|---|---|
| | | $F^-$ | $Cl^-$ | $NO_3^-$ | $PO_4^{-3}$ | $SO_4^{-2}$ |
| 1 | Al NASASHA | 2.200 | 536.680 | 7.890 | N.D | 1236.320 |
| 2 | Al JEERA | 2.790 | 1010.250 | 9.860 | N.D | 1082.490 |
| 3 | AL JEPANA | 5.460 | 2419.600 | 16.740 | N.D | 2332.160 |
| 4 | Al Nafeer | 3.610 | 728.040 | 9.540 | N.D | 598.550 |
| 5 | AL OWANAN | 2.070 | 616.880 | 8.590 | N.D | 1174.620 |

**Table ( 3.5 ) Results of cation analysis in the underground water sources in LIWA in mg/L before and after filtration using ICP.**

| well no. | Location | Before Feltration | | | | |
|---|---|---|---|---|---|---|
| | | $Na^{+}$ | $K^{+}$ | $Ca^{+2}$ | $Mg^{+2}$ | Total Fe |
| 1 | Al NASASHA | 565.900 | 51.000 | 269.800 | 93.000 | 0.600 |
| 2 | Al JEERA | 814.100 | 46.200 | 243.600 | 73.200 | 1.300 |
| 3 | AL JEPANA | 2350.000 | 74.200 | 189.400 | 80.200 | 0.420 |
| 4 | Al Nafeer | 2650.000 | 175.100 | 753.800 | 256.600 | 1.900 |
| 5 | AL OWANAN | 1200.400 | 56.200 | 560.000 | 70.200 | 0.400 |

| well no. | Location | After Filtration | | | | |
|---|---|---|---|---|---|---|
| | | $Na^{+}$ | $K^{+}$ | $Ca^{+2}$ | $Mg^{+2}$ | Total Fe |
| 1 | Al NASASHA | 426.400 | 22.600 | 286.600 | 55.900 | 0.900 |
| 2 | Al JEERA | 755.100 | 40.200 | 235.200 | 71.100 | 0.900 |
| 3 | AL JEPANA | 2010.100 | 78.400 | 300.100 | 79.400 | 0.900 |
| 4 | Al Nafeer | 596.300 | 36.700 | 107.900 | 35.900 | N.D |
| 5 | AL OWANAN | 318.900 | 42.100 | 220.100 | 56.100 | 0.300 |

**Table ( 3.6 ). Results of anion analysis in various samples of desalinated water sources in mg/L using IC.**

| No. | Location | Source | Anions in mg/l | | | | |
|---|---|---|---|---|---|---|---|
| | | | $F^-$ | $Cl^-$ | $NO_3^-$ | $PO_4^{-3}$ | $SO_4^{-2}$ |
| 1 | Abu Dhabi | Unit 2 / L 2006 | N.D. | 68.450 | N.D. | N.D | 8.500 |
| 2 | Abu Dhabi | Unit 2 / L 2006 | N.D. | 69.940 | N.D. | N.D | 9.220 |
| 3 | Abu Dhabi | Unit 2 / L 1006 | N.D. | 65.730 | N.D. | N.D | 9.340 |
| 4 | Abu Dhabi | Unit 1 / L 1006 | N.D. | 60.430 | N.D. | N.D | 6.220 |
| 5 | Abu Dhabi | Unit 4 / L 2008 | N.D. | 37.130 | N.D. | N.D | 5.330 |
| 6 | Bani Yas | Unit 4 / L 4100 | N.D. | 60.420 | N.D. | N.D | 8.61 |
| 7 | Bani Yas | New pump station | N.D. | 60.980 | N.D. | N.D | 8.680 |
| 8 | Bani Yas | Wathba pump station | N.D. | 70.370 | N.D. | N.D | 9.490 |
| 9 | Bani Yas | Unit 4 / L 4200 | N.D. | 65.980 | N.D. | N.D | 8.770 |
| 10 | Marfaa | MR 6 / L 300 | N.D. | 51.110 | N.D. | N.D | 7.200 |
| 11 | Shahama | Unit 3 / L 3102 | N.D. | 58.750 | N.D. | N.D | 8.030 |

**Table ( 3.7 ). Results of cation analysis in various samples of disalinated water sources in mg/L using ICP.**

| No. | Location | Source | Cations in mg/l | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $Na^{+}$ | $K^{+}$ | $Ca^{++}$ | $Mg^{++}$ | Total Fe | $Al^{+++}$ | $Cr^{+++}$ |
| 1 | Abu Dhabi | Unit 2 / L 2006 | 45.840 | 3.880 | 5.490 | 4.060 | 0.200 | N.D | N.D |
| 2 | Abu Dhabi | Unit 2 / L 2006 | 42.280 | 3.660 | 7.640 | 4.050 | 0.170 | N.D | N.D |
| 3 | Abu Dhabi | Unit 2 / L 1006 | 38.130 | 3.530 | 7.050 | 3.990 | 0.080 | N.D | N.D |
| 4 | Abu Dhabi | Unit 1 / L 1006 | 28.310 | 1.770 | 6.460 | 1.380 | 0.930 | N.D | N.D |
| 5 | Abu Dhabi | Unit 4 / L 2008 | 21.920 | 2.020 | 5.590 | 2.040 | 0.200 | N.D | N.D |
| 6 | Bani Yas | Unit 4 / L 4100 | 33.320 | 3.090 | 8.980 | 3.810 | N.D | N.D | N.D |
| 7 | Bani Yas | New pump station | 33.610 | 3.400 | 9.400 | 3.710 | N.D | N.D | N.D |
| 8 | Bani Yas | Wathba pump station | 44.150 | 4.100 | 13.070 | 4.610 | N.D | N.D | N.D |
| 9 | Bani Yas | Unit 4 / L 4200 | 32.200 | 3.150 | 9.160 | 3.690 | 0.100 | N.D | N.D |
| 10 | Marfaa | MR 6 / L 300 | 35.150 | N.D | 18.410 | N.D | N.D | N.D | N.D |
| 11 | Shahama | Unit 3 / L 3102 | 35.080 | 2.900 | 9.330 | 3.810 | N.D | N.D | N.D |

## 3.2. Determination of Fluoride in Tea

Because UAE is considered as a tea drinking nation, a habit that would account for a substantial increase in fluoride consumption. I undertook a survey of $F^-$ level in several commercially available teas from different regions. The $F^-$ concentration level was determined in tea infusions by using FISE in the presence of TISAB II buffer which is considered an effective and easy to use potentiometric technique for $F^-$ determination in a wide variety of samples in aqueous solution. As well some detailed studies were considered such as the effect of infusion time on the extracted $F^-$ concentration level and the difference between the infusion and boiling procedure for extraction of $F^-$ from the sample under investigation.

### 3.2.1. Fluoride Content of Tea:

The fluoride content of 4 types of tea brands are determined using FISE and shown in table 3.8. These brands are Lipton, Brooke Bond, Leone and Al Wazza. The highest content of fluoride is found in Lipton tea which is 4.3 mg/L or 214 mg/kg which corresponds to 0.428 mg/tea bag or per 2 gm of tea. The minimum content of fluoride which is 0.914 mg/L or 0.091 mg/tea bag is found in Al Wazza tea brand. The average content of fluoride in the tea types studied is 2.33 mg/L. It can be claimed that tea is a good source of fluoride intake. The fluoride content of tea versus infusion time is shown in table 3.9 and Fig. 3.20 for the "Lipton brand". The amount of extracted fluoride increases with infusion time till 11 minutes, after this, there is a plateau as the amount extracted in

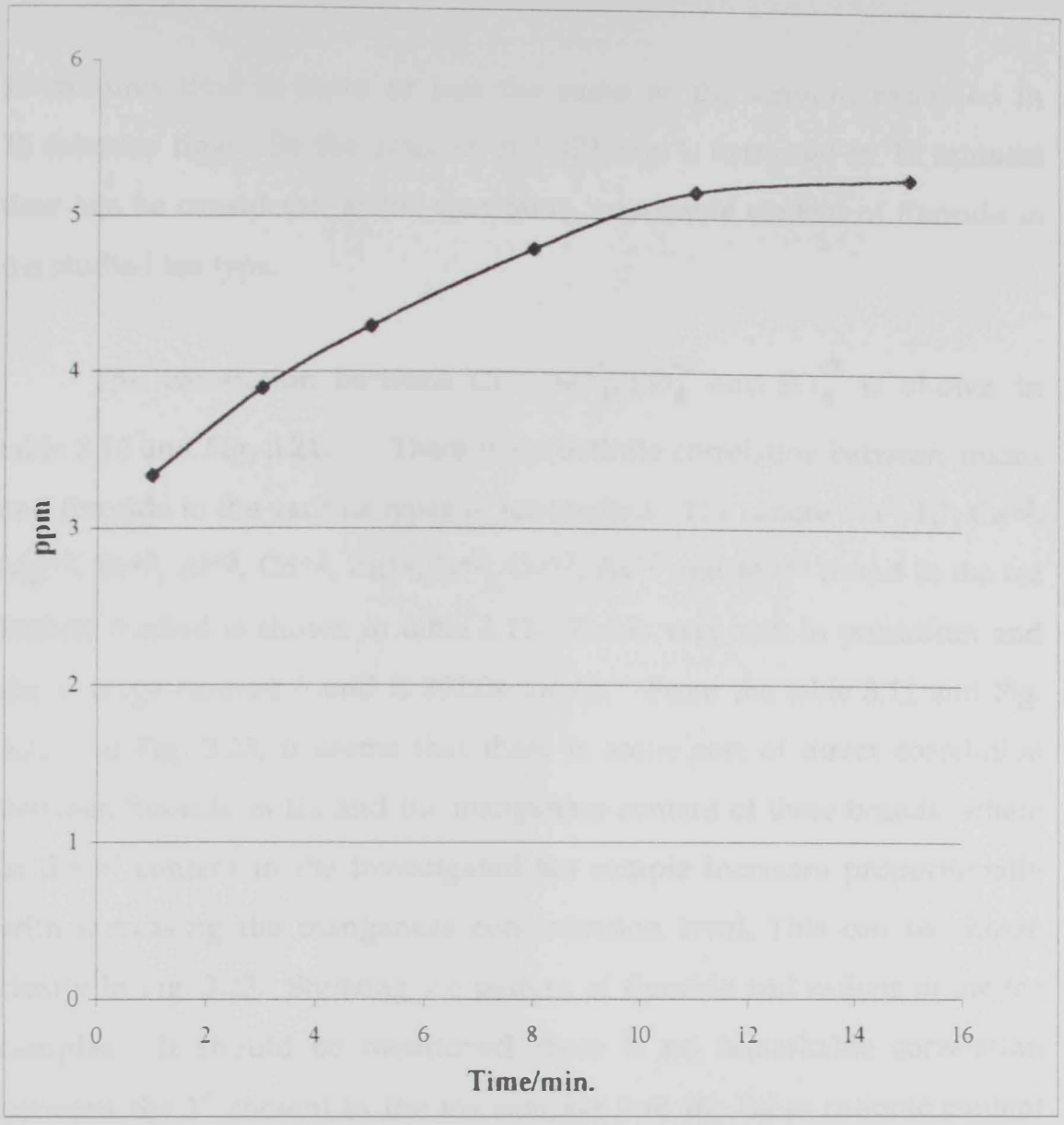


**Fig. 3.20 Variation of $F^-$ content with infusion time in Lipton tea bag.**

11 minutes time is more or less the same as the amount extracted in 15 minutes time. So the amount of 5.171 mg/L extracted in 11 minutes time can be considered as the maximum reasonable content of fluoride in the studied tea type.

The correlation between $Cl^-$, $NO_3^-$, $PO_4^{-3}$ and $SO_4^{-2}$ is shown in table 3.10 and Fig. 3.21. . There is no definite correlation between anions and fluoride in the various types of tea studied. The cations $Na^+$, $K^+$, $Ca^{+2}$, $Mg^{+2}$, $Fe^{+3}$, $Al^{+3}$, $Cd^{+2}$, $Zn^{+2}$, $Si^{+2}$, $Cu^{+2}$, $As^{+3}$ and $Mn^{+2}$ found in the tea brands studied is shown in table 3.11. Tea is very rich in potassium and the average amount found is 392.04 mg/L. From the table 3.11 and Fig. 3.22 and Fig. 3.23, it seems that there is some sort of direct correlation between fluoride in tea and the manganese content of these brands, where as the $F^-$ content in the investigated tea sample increases proportionally with increasing the manganese concentration level. This can be shown clearly in Fig. 3.23. Showing the pattern of fluoride and cations in the tea samples. It should be mentioned there is no remarkable correlation between the $F^-$ content in the tea samples and the other cationic content e.g. $Al^{3+}$, $Ca^{2+}$ and $Na^+$.

Many trials were done for determination of $F^-$ in the various tea samples using IC technique (Fig. 3.24) and results obtained vary between 31.51 mg/L and 47.625 mg/L or 2.913 mg/tea bag and 4.7098 mg/tea bag. These results differed from the results obtained using-ISE for the same tea

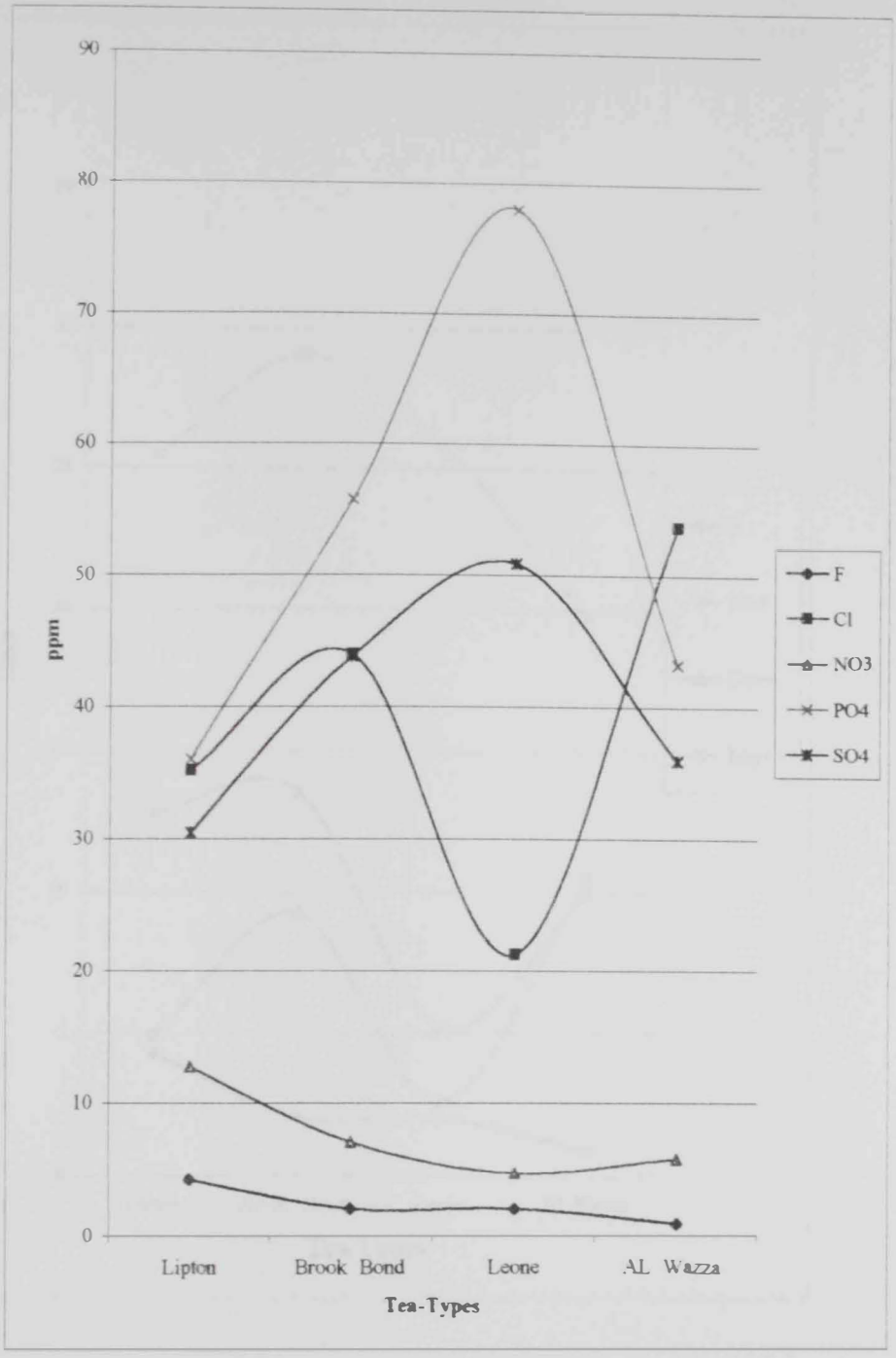


**Fig.3.21 Comparison between $F^-$ concentration level and the other anions in some tea samples**

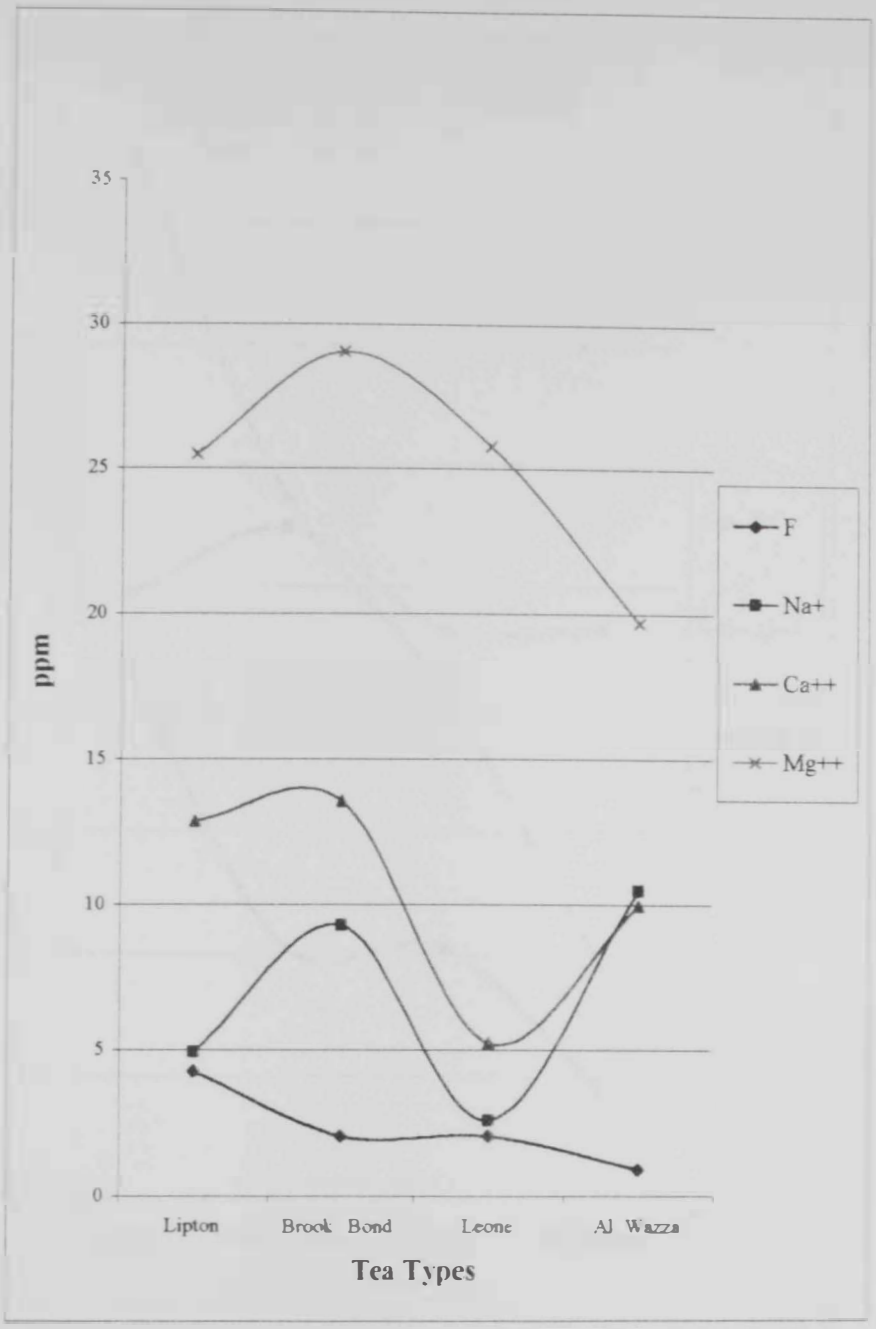


**Fig. 3.22 Pattern between F concentration level and $Na^{+}$,$Ca^{+2}$,$Mg^{+2}$ cations in tea samples**

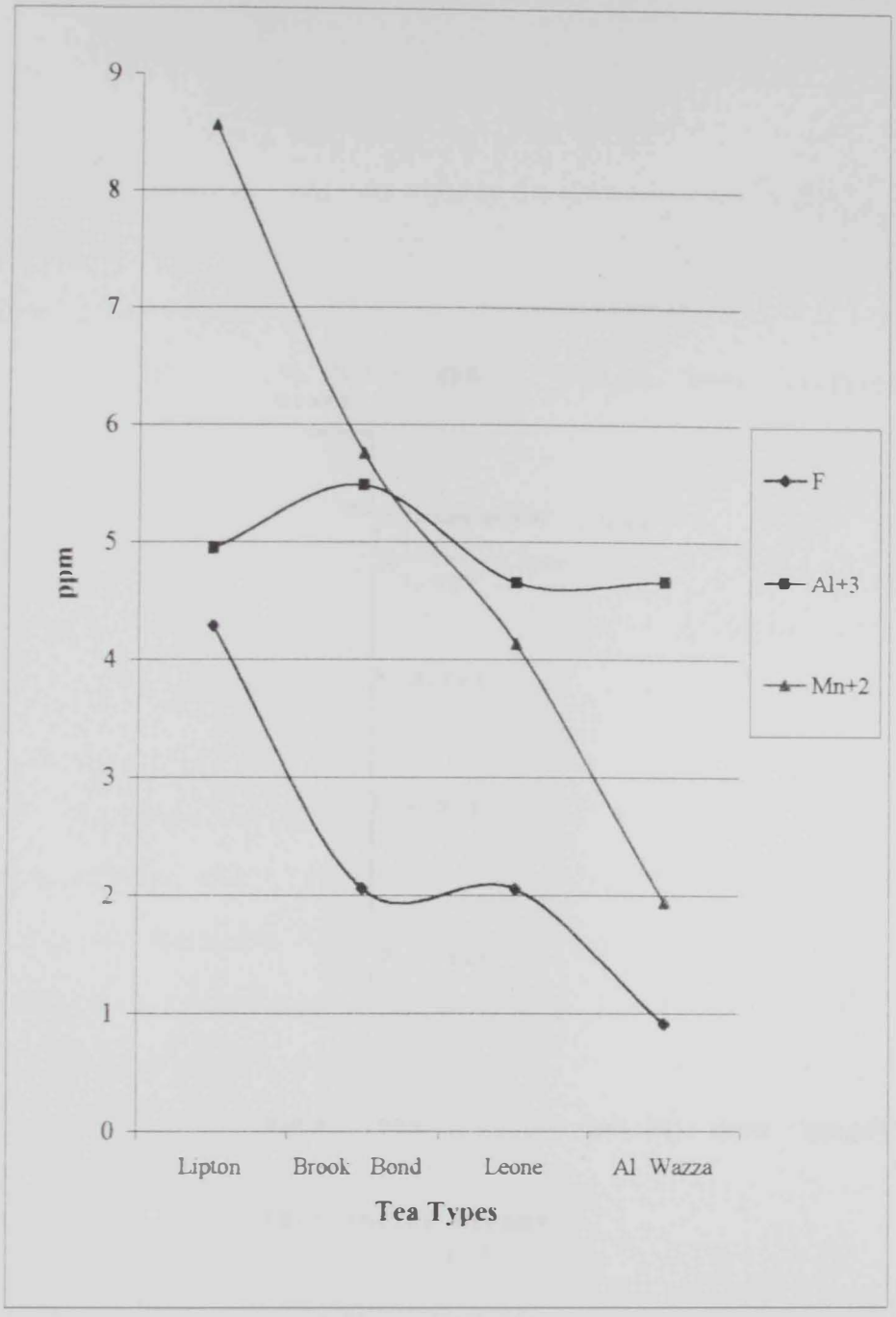


**Fig. 3.23 Pattern between F concentration level and $Al^{+3}$, $Mn^{+2}$ cations in tea samples**

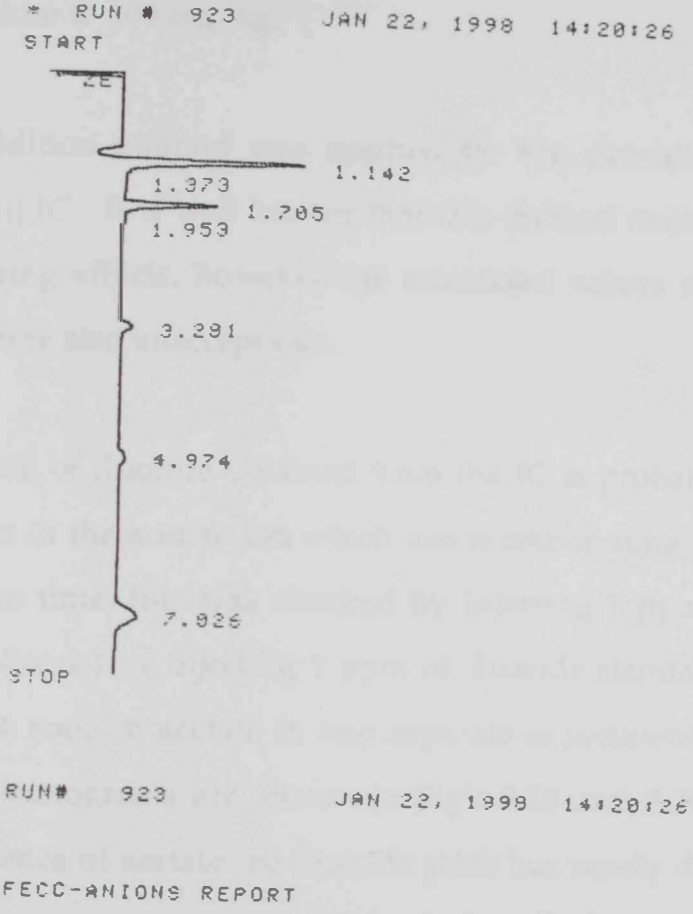


Fig. 3.24. IC chromatogram for the infused Lipton (tea bag) solution 25-fold diluted using $CO_3^{-2}/HCO_3^-$ eluent solution.

types which vary between 0.914 mg/L and 4.289 mg/L or 0.091 mg/tea bag and 0.428 mg/tea bag. Moreover, the IC results of analysis of $F^-$ content in the tea samples are very high in comparison to the corresponding previously reported results (WHO, 1996). The FISE results are more or less identical to results of $F^-$ content determined in the same types of tea samples, which is close to 100 mg/kg.

Standard addition method was applied for the determination of fluoride in tea using IC. It is well known that this method overcomes the problem of interfering effects, however the calculated values of fluoride ion in tea (mg/L) were also unacceptable.

The high value of fluoride obtained from the IC is probably due to the interfering effect of the acetate ion which has retention time very close to fluoride retention time, this was checked by injecting 1 ppm fluoride standard into IC followed by injecting 1 ppm of fluoride standard spiked with 0.05 ml of 15% sodium acetate in two separate experiments and the corresponding chromatograms are shown in Fig's 3.25 and 3.26. It was noticed that in presence of acetate the fluoride peak has nearly doubled in size and so the fluoride concentration obtained also doubled. This result confirms the incompatibility of the IC technique for determination of fluoride ion in the presence of acetate ion. As we mentioned above the IC chromatograms for the various tea samples indicate that there is a possibility for the presence of acetate ion in tea solution. Therefore, we can not use the IC technique for $F^-$ determination in tea samples.

It should be mentioned that the effect of boiling procedure of the tea bag in water, instead of infusion method, on the released $F^-$ into solution was checked. It was found that boiling of the Lipton tea bag in a definite volume of water (100 ml) for 2 min, gives 282.11 mg/kg $F^-$ concentration which is higher than the corresponding value using infusion technique by about 38%. Also, the effect of addition of charcoal on the extraction of $F^-$ from Lipton tea bag was considered. Addition of 1 g or 2 g charcoal to the tea solution leads to loss in the $F^-$ concentration by 11%. This result could be explained by the adsorption of $F^-$ at the charcoal surface. The $F^-$ content in the latter two experiments was measured using FISE method.

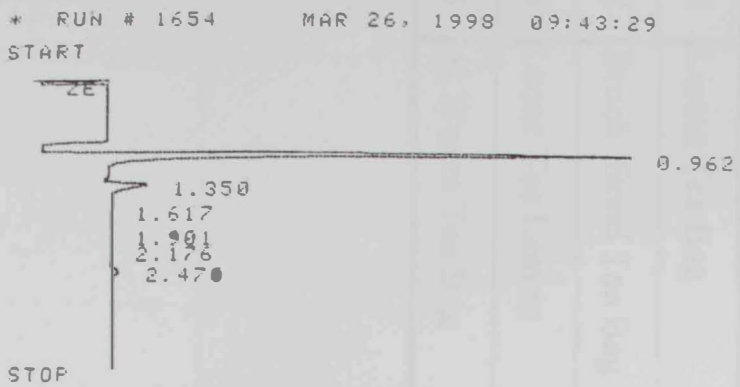


Fig. 3.25. Ion chromatogram of 1.0 ppm standard $F^-$ solution using $CO_3^{2-}$ /$HCO_3^-$ eluent solution.

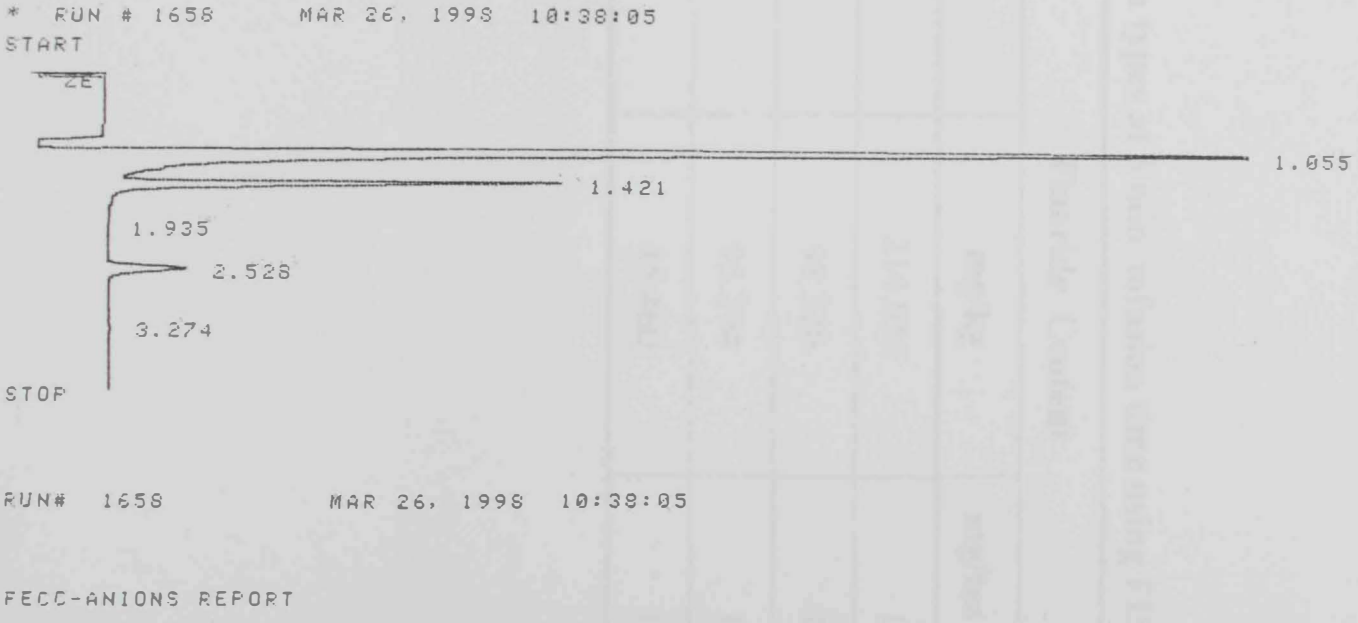


Fig. 3.26. Ion chromatogram of 1.0 ppm standard $F^-$ solution in presence of 0.75 mg/L acetate ion using $CO_3^{2-}$ /$HCO_3^-$ eluent solution.

**Table ( 3.8 ). Results of $F^-$ determination in the various tea types at 5 min. infusion time using FISE**

| No. | Tea Type | Source | Fluoride Content | | |
|---|---|---|---|---|---|
| | | | mg/l | mg/kg | mg/tea bag (2gm) |
| 1 | Lipton Tea Bag | India | 4.290 | 214.056 | 0.428 |
| 2 | Brook Bond Tea Bag | India | 2.065 | 98.320 | 0.197 |
| 3 | Leone Tea Leaves | India | 2.061 | 95.294 | 0.191 |
| 4 | Al Wazza Tea Bag | Seri Lanka | 0.914 | 45.460 | 0.091 |

**Table (3.9). Results of extracted $F^-$ with infusion time in Lipton tea bag.**

| Infusion time/min. | Flouride Content | | |
|---|---|---|---|
| | mg/l | mg/kg | mg/tea bag (2gm) |
| 1 | 3.334 | 166.354 | 0.333 |
| 3 | 3.894 | 194.282 | 0.389 |
| 5 | 4.290 | 214.056 | 0.428 |
| 8 | 4.795 | 239.250 | 0.479 |
| 11 | 5.171 | 258.026 | 0.516 |
| 15 | 5.262 | 262.562 | 0.525 |

**Table ( 3.10 ) Results of anion analysis in the various tea types at 5 min. infusion time in mg /L using IC .**

| N0. | Tea Type | Anions in mg/l | | | | |
|---|---|---|---|---|---|---|
| | | $F^-$ | $Cl^-$ | $NO_3^-$ | $PO_4^{-3}$ | $SO_4^{-2}$ |
| 1 | Lipton | 4.290 | 35.200 | 12.760 | 36.035 | 30.450 |
| 2 | Brook Bond | 2.065 | 43.966 | 7.113 | 55.780 | 43.850 |
| 3 | Leone | 2.061 | 21.280 | 4.769 | 78.010 | 50.902 |
| 4 | AL Wazza | 0.914 | 53.740 | 5.825 | 43.280 | 35.960 |

$F^-$ determined using FISE

**Table ( 3.11 ). Results of cation analysis in the various tea types at 5 min. infusion time using ICP.**

| No. | Tea Type | Cations in mg/l | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $Na^{+}$ | $k^{+}$ | $Ca^{++}$ | $Mg^{++}$ | Total Fe | $Al^{+++}$ | $Cd^{++}$ | $Zn^{++}$ | $Si^{+4}$ | $Cu^{++}$ | $As^{+++}$ | $Mn^{++}$ |
| 1 | Lipton | 4.946 | 306.900 | 12.854 | 25.499 | 1.325 | 4.946 | - | 0.304 | 0.621 | 0.156 | - | 8.560 |
| 2 | Brook Bond | 9.289 | 419.110 | 13.550 | 29.060 | N.D | 5.486 | N.D | 0.390 | 0.628 | 0.225 | N.D | 5.758 |
| 3 | Leone | 2.600 | 462.700 | 5.250 | 25.800 | 0.113 | 4.650 | N.D | 0.412 | 0.710 | 0.383 | N.D | 4.136 |
| 4 | Al Wazza | 10.479 | 379.460 | 9.959 | 19.710 | N.D | 4.663 | N.D | 0.281 | 0.310 | 0.251 | N.D | 1.941 |

## 3.3. Determination of Fluoride in Honey

Fluoride is naturally occurring in different types of food such as honey. In this context fluoride content in some samples of honey was quantitatively determined. Some trials were made for fluoride determination in honey samples using IC. The IC chromatogram of honey shows a very high sharp peak at retention time identical to $F^-$ retention time (Fig. 3.27). The calculated $F^-$ content in honey using the IC is very high and unacceptable amount (8.298 - 24.612 mg/L). These results reveal that the IC peak is probably not corresponding to $F^-$ peak only and it may be overlapped with other organic anion peak e.g. acetate ion peak. These results are more or less close to the IC behaviour of infused tea solution. It can be concluded that the IC technique is not a suitable technique for determination of $F^-$ content in honey solution.

The fluoride levels in the four honey samples were determined by using FISE. The dissolved honey solution sample was diluted with TISAB II buffer solution and subjected directly to the FISE of the calibrated ionic analyzer.

The amount of fluoride was found in various samples of honey is shown in Table 3.12. Honey can be considered as relatively high source of fluoride as shown from analysis of the samples. Germany (Langenese) and Yemen have approximately the same $F^-$ content, i.e. 0.5875 mg/kg and 0.5973 mg/kg respectively (Table 3.12). However, one sample from Sudan contains no fluoride and a sample from Saudi Arabia contains only

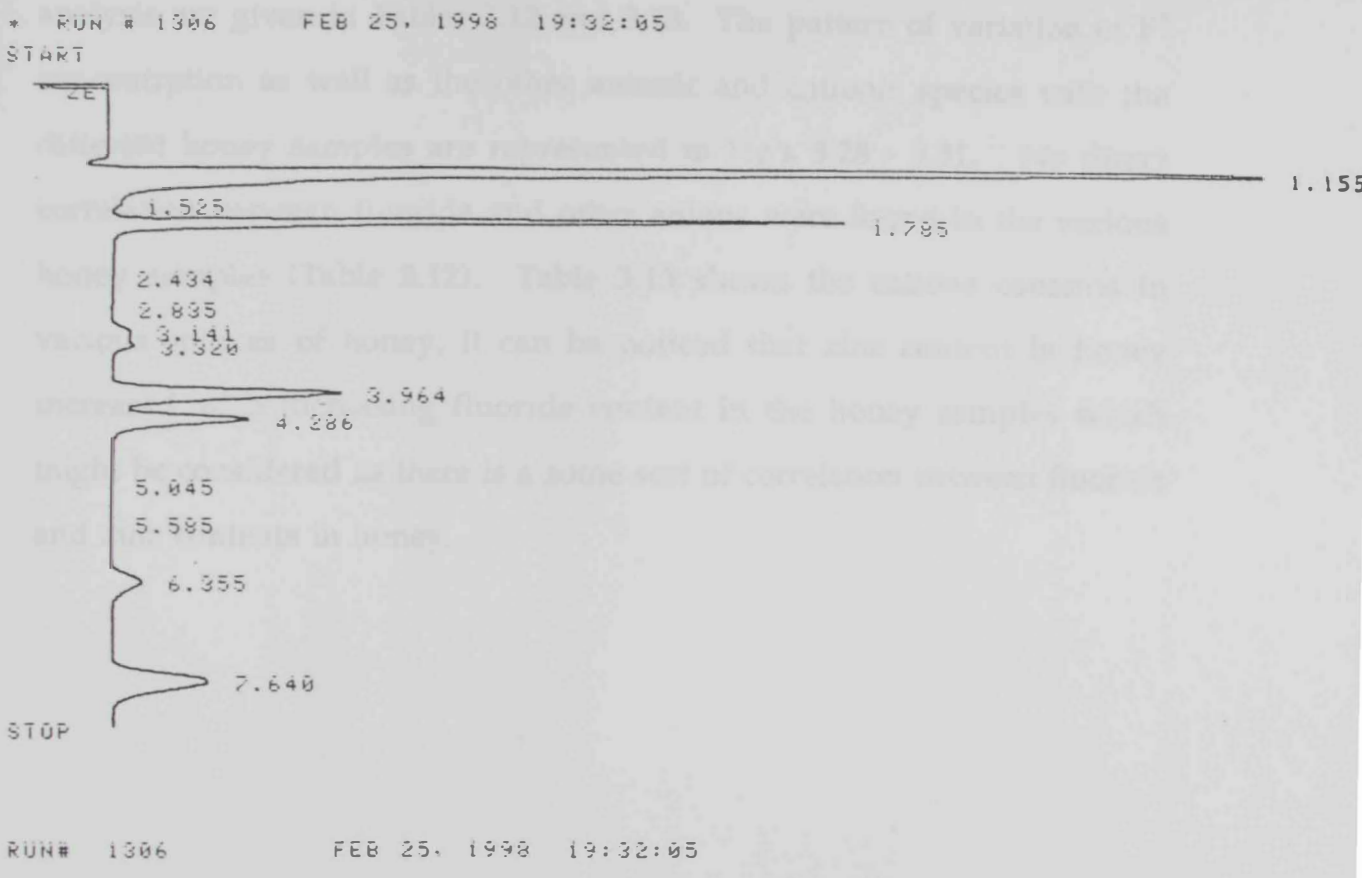


Fig. 3.27. The IC chromatogram of diluted honey solution (2 gm in 100 ml deionized water) using $CO_3^{2-}/HCO_3^-$ eluent solution.

0.072 mg/kg. The average amount of fluoride in honey is 0.314 mg/kg which can be considered as a reasonable amount of fluoride.

The different honey samples were subjected to full cationic and anionic analysis using ICP and IC techniques, respectively. The results of analysis are given in Tables 3.12 and 3.13. The pattern of variation of $F^-$ concentration as well as the other anionic and cationic species with the different honey samples are represented in Fig's 3.28 - 3.31. No direct correlation between fluoride and other anions were found in the various honey samples (Table 3.12). Table 3.13 shows the cations contents in various sources of honey, it can be noticed that zinc content in honey increased with increasing fluoride content in the honey samples which might be considered as there is a some sort of correlation between fluoride and zinc contents in honey.

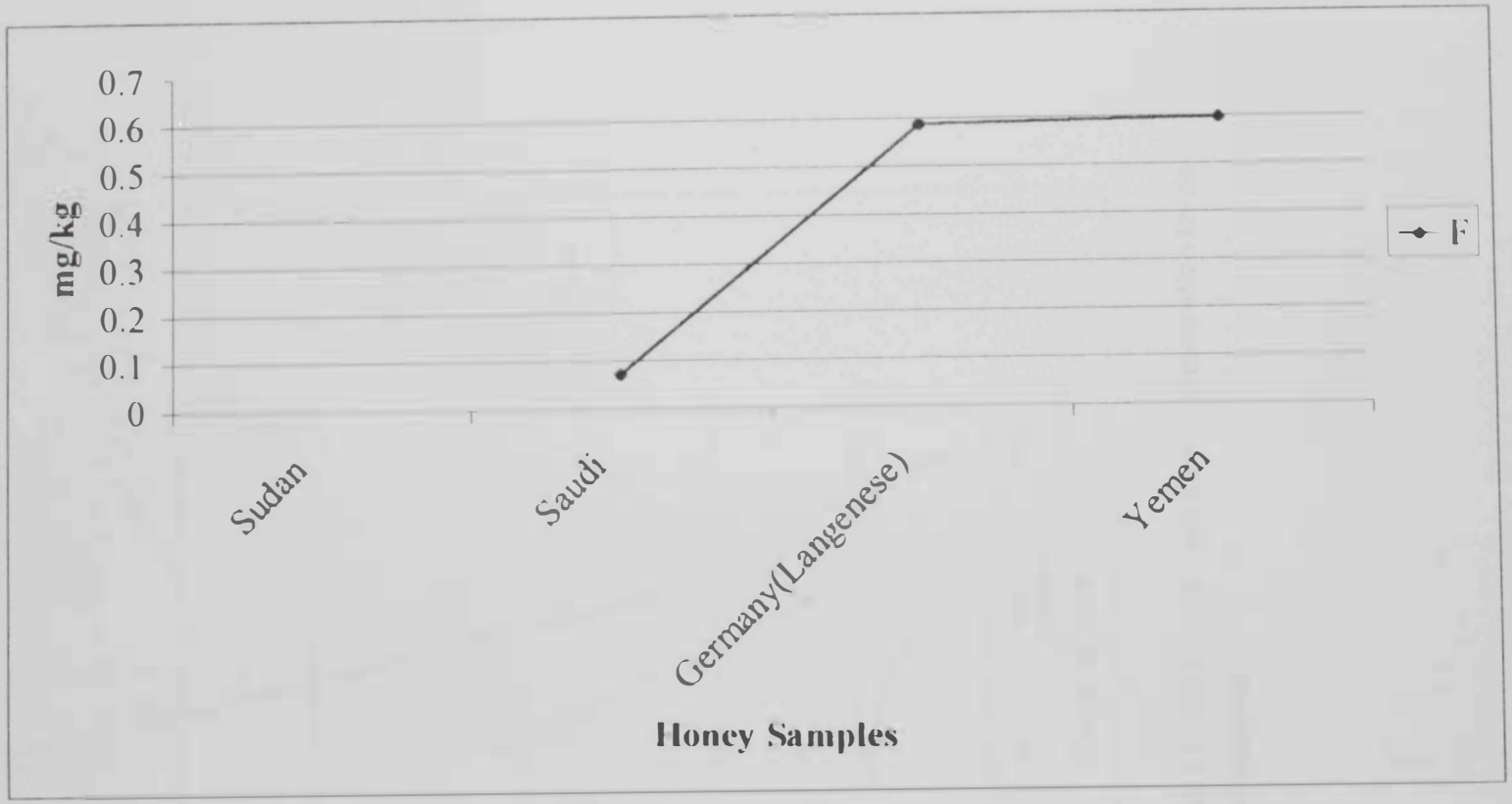


**Fig. 3.28 Variation of F concentration level in the different honey samples .**

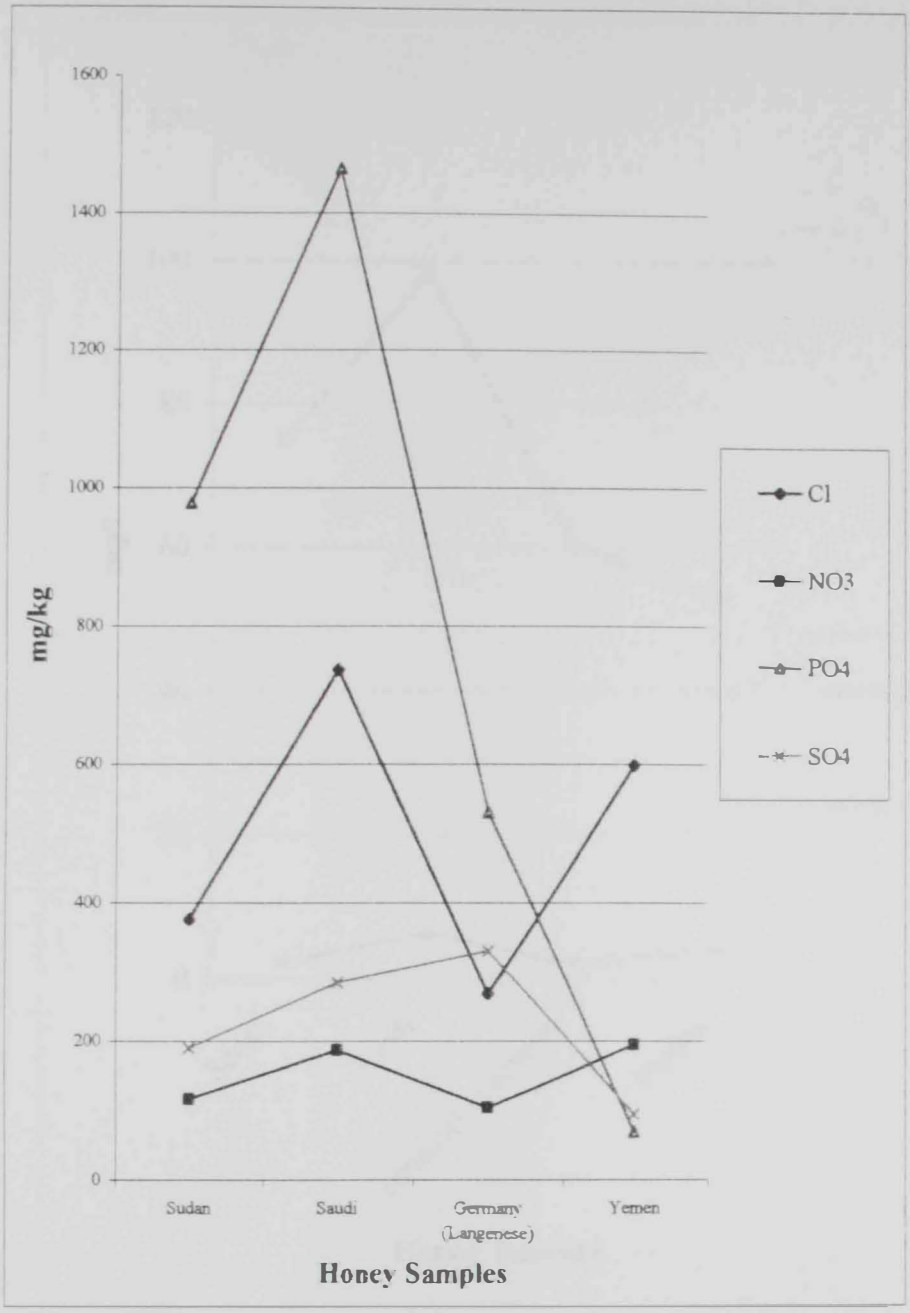


**Fig. 3.29 Variation of $Cl^-$, $NO3^-$, $PO4^{-3}$ and $SO4^{-2}$ concentration levels in the different honey samples.**

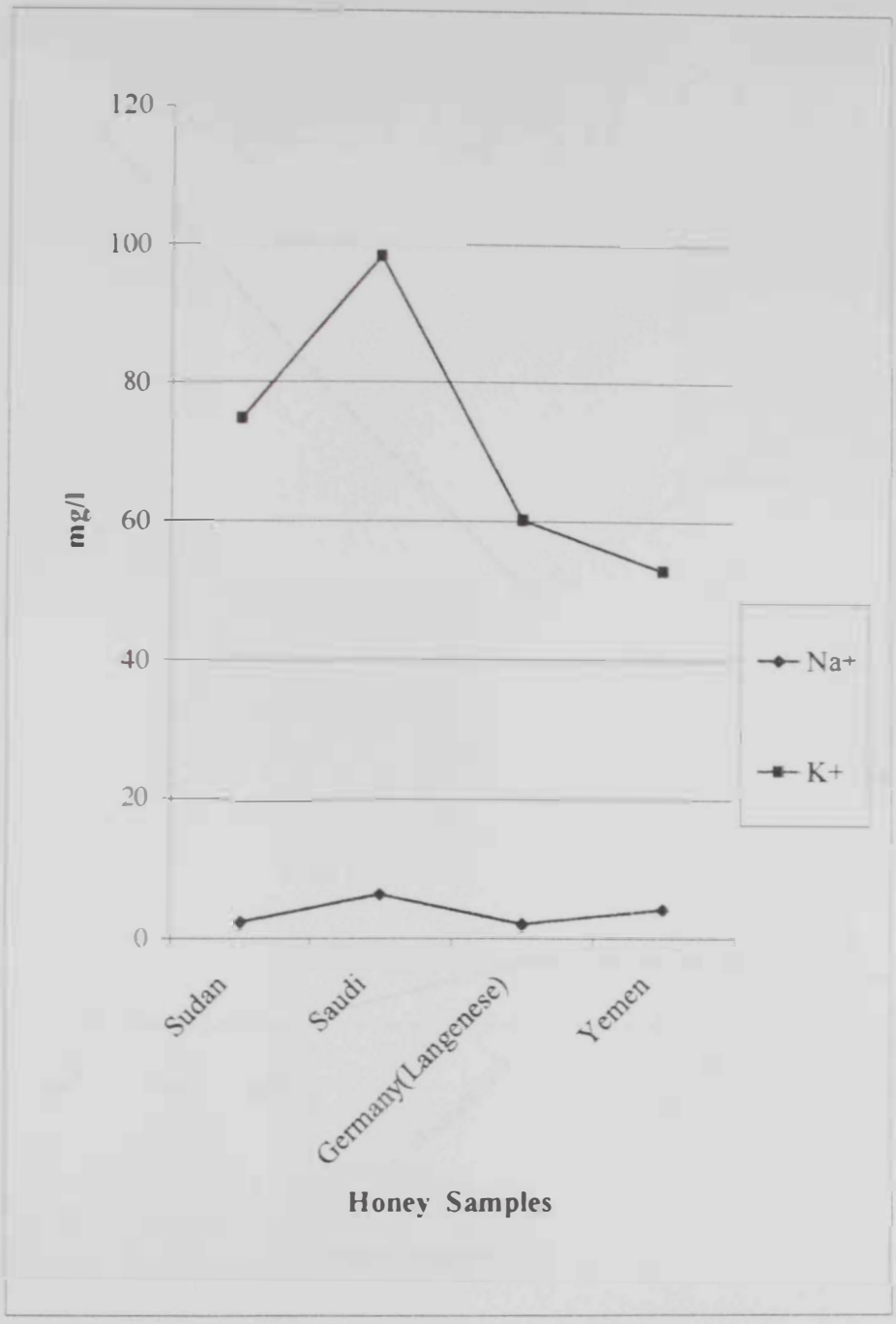


**Fig. 3.30 Variation of $Na^+$ and $K^+$ concentration levels in the different honey samples.**

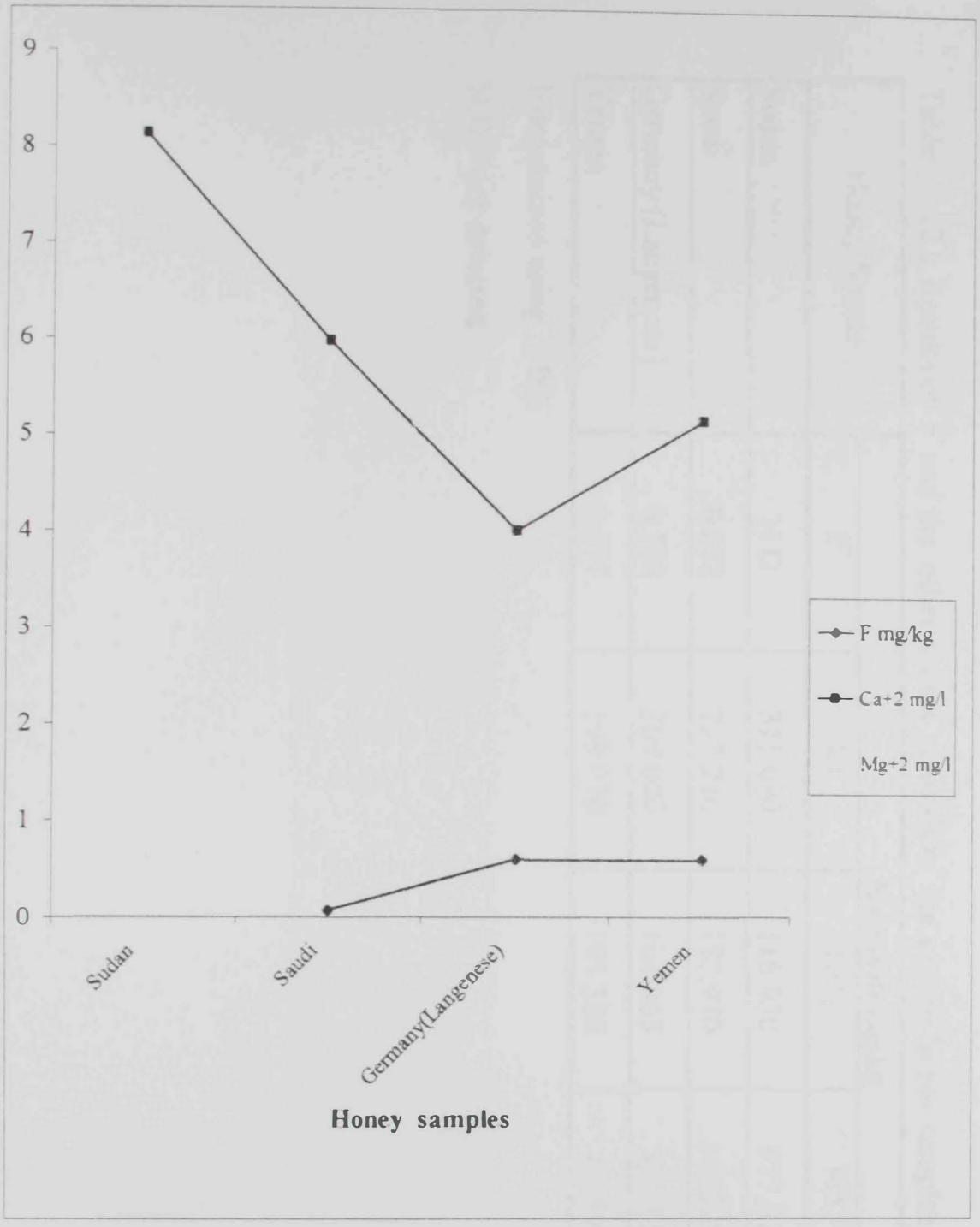


**Fig.3.31 Variation of $F^-$ concentration level with $Ca^{+2}$ and $Mg^{+2}$ concentrations in the different honey samples**

Table ( 3.12 ). Results of $F^-$ and the other anions analysis in the various honey samples using IC.

| Honey Source | Anions in mg/kg | | | | |
|---|---|---|---|---|---|
| | $F^-$ | $Cl^-$ | $NO_3^-$ | $PO_4^{-3}$ | $SO_4^{-2}$ |
| Sudan | N.D | 375.690 | 116.930 | 977.970 | 190.900 |
| Saudi | 0.072 | 737.240 | 187.970 | 1465.200 | 284.990 |
| Germany (Langenese) | 0.588 | 269.000 | 104.665 | 531.131 | 331.220 |
| Yemen | 0.597 | 599.020 | 195.380 | 69.590 | 95.050 |

$F^-$ determined using FISE

N.D = not detected

**Table ( 3.13 ). Results of cation analysis in the various honey samples in mg/l using ICP.**

| Honey source | Cations in mg/l | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Na^{+}$ | $K^{+}$ | $Ca^{++}$ | $Mg^{++}$ | Total Fe | $Al^{+++}$ | $Cd^{++}$ | $Zn^{++}$ | $Si^{+4}$ | $Cu^{++}$ | $As^{+++}$ | $Mn^{++}$ |
| **Sudan** | 2.323 | 74.750 | 8.129 | 4.130 | N.D. | N.D. | N.D. | 0.152 | 0.554 | 0.090 | N.D. | N.D. |
| **Saudi** | 6.360 | 98.230 | 5.970 | 6.869 | N.D. | 0.190 | N.D. | 0.160 | 0.485 | 0.072 | N.D. | N.D. |
| **Germany(Langenese)** | 2.129 | 60.100 | 4.000 | 2.899 | N.D. | 0.070 | N.D. | 0.148 | 0.808 | 0.106 | N.D. | 0.040 |
| **Yemen** | 4.214 | 52.920 | 5.156 | 2.786 | N.D. | N.D. | N.D. | 0.253 | 0.478 | 0.046 | N.D. | N.D. |

N.D. = Not Detected.

## 3.4. Determination of Fluoride in Juice Samples

The juice solutions are mostly acidic solutions. It is well known that IC analysis can not be applied for analysis of acidic solutions. Therefore, the fluoride ion concentration level in some juice samples was determined using FISE in the presence of TISAB (II) buffer solution (experimental section, page 46). The results of Fluoride contents of some juice types are listed in table 3.14. It was found that the amount of fluoride content is in the range of 0.02 mg/L in orange juice to 0.17 mg/L in grape juice and the average content of fluoride in the various investigated samples is 0.07809 ± 0.0442 mg/L. It should be mentioned that the source of $F^-$ in these juice samples is the natural fruits, whereas the investigated samples are concentrated natural juice solutions. From the above reported values (Table 3.14) we can not consider the fruit juices are not a good source for fluoride intake.

The full anionic analysis of the investigated juice samples was not carried out using the IC technique because of the acidic character of the juice solutions. In order to investigate if there is any correlation between the cationic content of the various juice samples and $F^-$ content, the cationic contents of the various samples were analyzed using ICP-ES. The results of cations analysis in the various juice samples are shown in table (3.15). The fruit juices are very rich in potassium content, which is in the range of 242 mg/L $K^+$ in mango juice to 1198 mg/L $K^+$ in apple juice. The average content of $K^+$ in the sample is 896 mg/L $K^+$.

Generally, the average values of the sodium, calcium and magnesium contents are 91 mg/L, 91.2 mg/L and 88.5 mg/L, respectively. Total iron content in the juice sample was not detected, however $Al^{3+}$ was found in the range of 0.4 mg/L $Al^{3+}$ in orange juice to 1.41 mg/L $Al^{3+}$ in guava juice. There is some samples contains a relatively high content of silicon e.g. pineapple juice that contain 46.15 mg/L $Si^{4+}$. Figures 3.32-3.35 show the variation of some cations content in the sample under investigation as well as the variation of $F^-$ content. However, there is no direct correlation between the $F^-$ content and the other cations content in the samples. Fig. 3.33 shows that both $Ca^{2+}$ and $Mg^{2+}$ are possibly in a double salt form and both are varied in more or less as the $F^-$ content varied in the various juice samples.

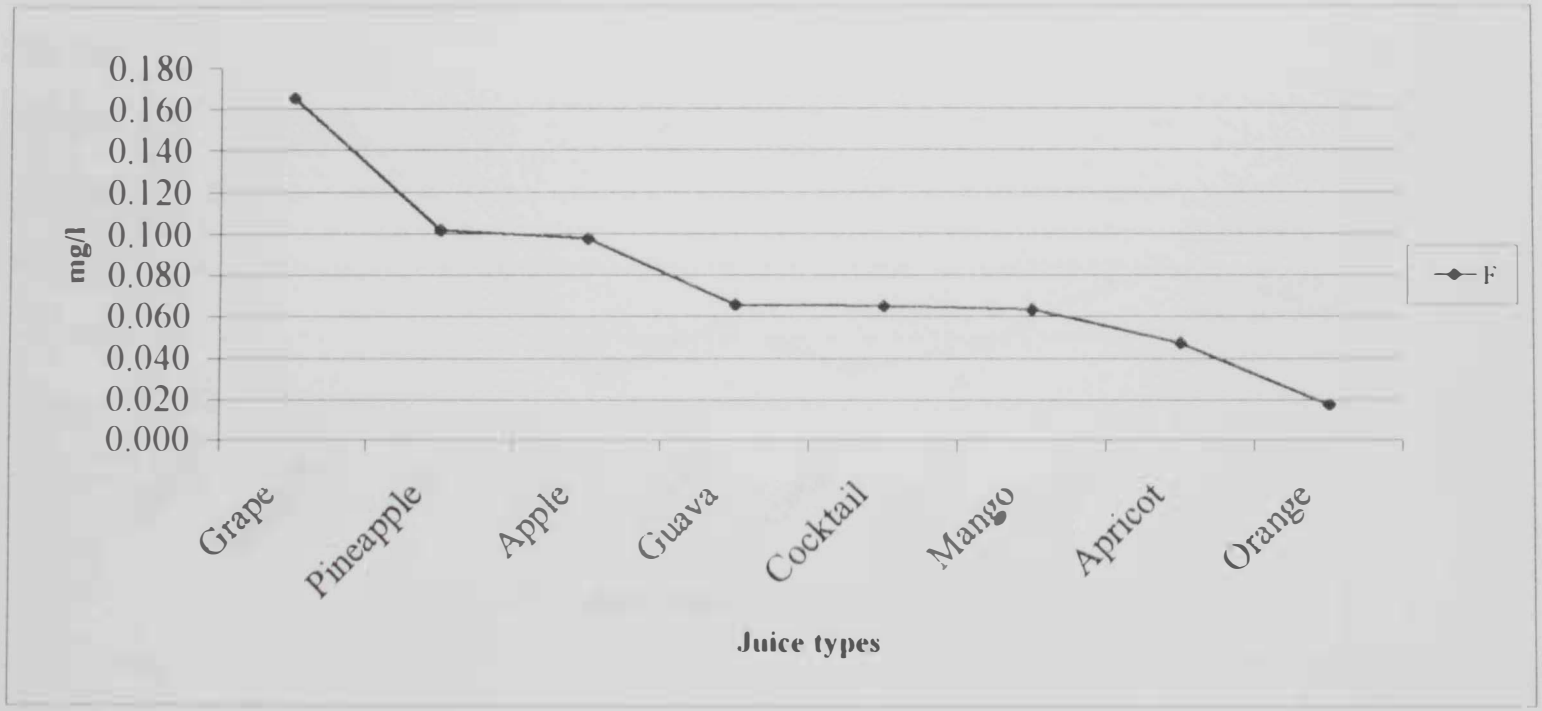


**Fig.3.32 Pattern of F concentration level in the various types of juices .**

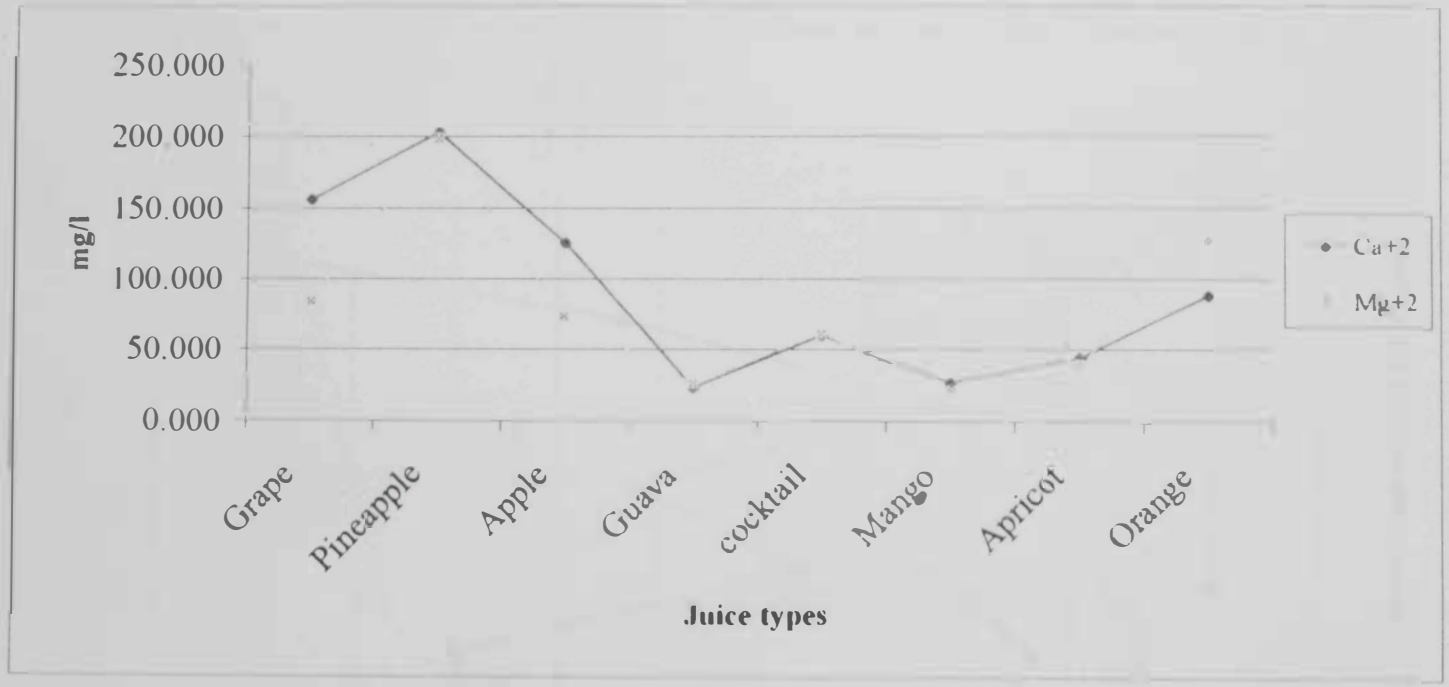


**Fig. 3.33 Variation of $Ca^{+2}$ and $Mg^{+2}$ concentration levels in the various types of juices .**

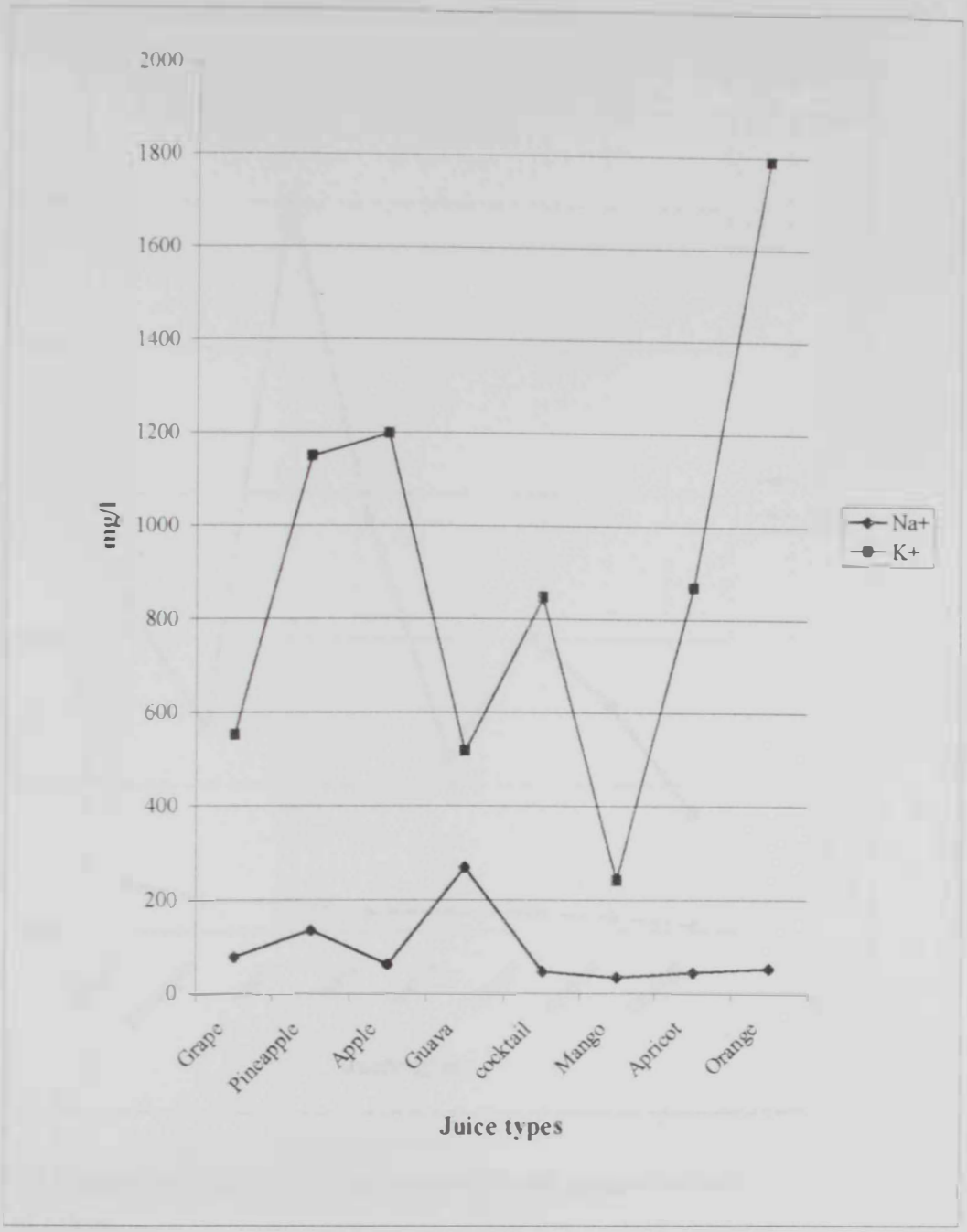


**Fig.3.34 Variation of $Na^+$ and $K^+$ concentration levels in the various types of juices .**

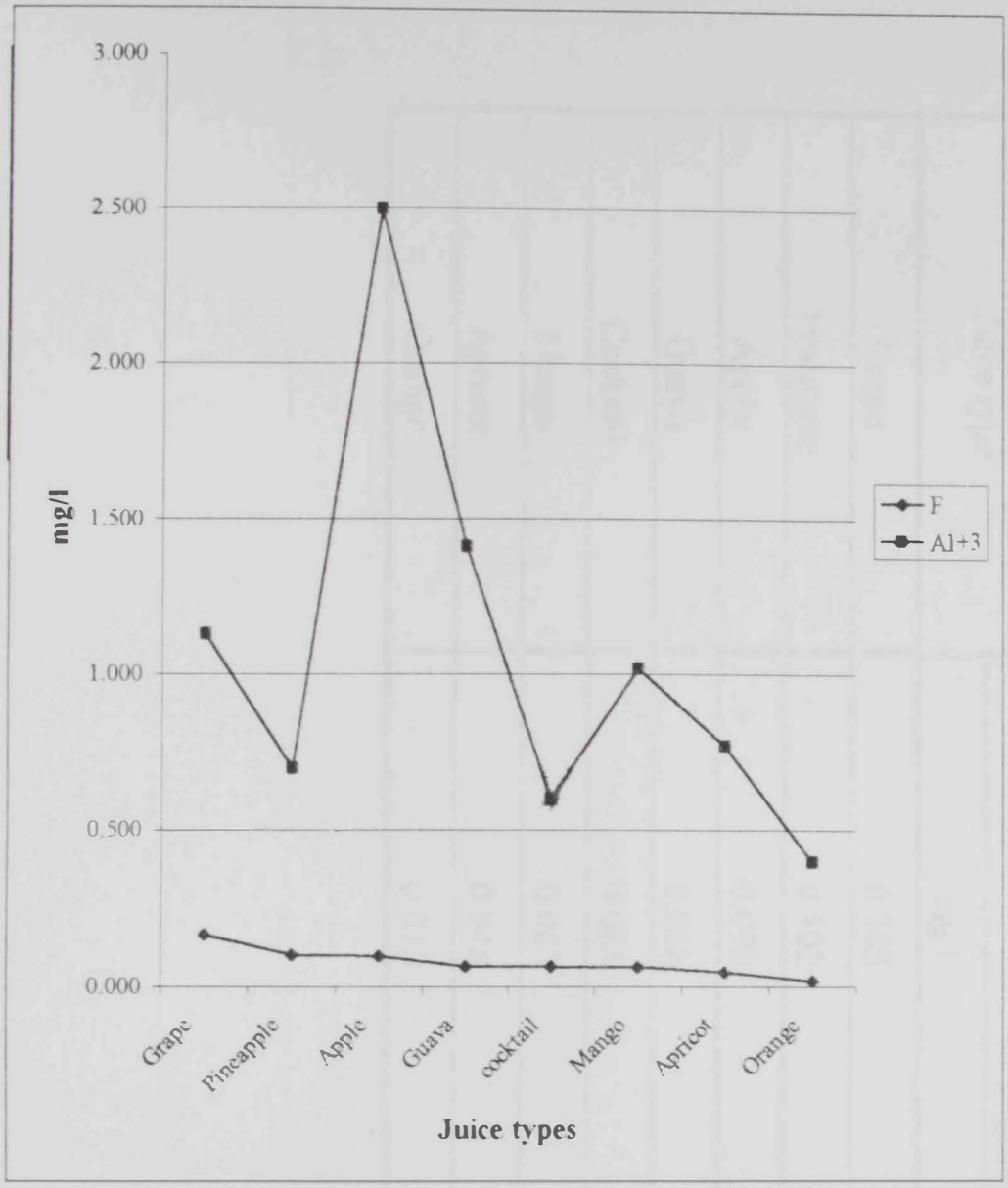


**Fig. 3.35 Pattern of F and $Al^{+3}$ concentration levels in the various types of juices .**

Table ( 3.14 ) Results of $F^-$ determination in various juice types using FISE .

| Juice type | Fluoride content | |
|---|---|---|
| | mg/l | mg/200ml |
| Grape | 0.165 | 0.033 |
| Pineapple | 0.102 | 0.020 |
| Apple | 0.098 | 0.020 |
| Guava | 0.066 | 0.013 |
| Cocktail | 0.065 | 0.013 |
| Mango | 0.063 | 0.013 |
| Apricot | 0.048 | 0.010 |
| Orange | 0.018 | 0.004 |

**Table (3.15 ) . Results of cation analysis in the various juice types in mg/l using ICP .**

| Juice type | Cations in mg/l | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $Na^{+}$ | $K^{+}$ | $Ca^{++}$ | $Mg^{++}$ | Total Fe | $Al^{+++}$ | $Cd^{++}$ | $Zn^{++}$ | $Si^{+4}$ | $Cu^{++}$ | $As^{+++}$ | $Mn^{++}$ |
| **Grape** | 77.800 | 552.700 | 156.700 | 84.630 | 12.100 | 1.130 | N.D | 0.550 | 11.100 | 1.140 | N.D | 0.680 |
| **Pineapple** | 135.700 | 1150.100 | 203.200 | 199.000 | 0.300 | 0.700 | N.D | 0.970 | 46.150 | 1.000 | N.D | 26.100 |
| **Apple** | 62.900 | 1197.800 | 126.000 | 72.600 | 2.050 | 2.500 | N.D | 0.550 | 9.940 | 1.830 | N.D | N.D |
| **Guava** | 270.000 | 518.000 | 23.630 | 26.200 | 1.000 | 1.410 | N.D | 0.500 | 3.680 | 1.330 | N.D | 0.160 |
| **cocktail** | 47.300 | 848.100 | 59.800 | 61.100 | N.D | 0.600 | N.D | 0.520 | 10.440 | 1.210 | N.D | 1.020 |
| **Mango** | 34.300 | 242.200 | 27.400 | 21.700 | N.D | 1.020 | N.D | 0.300 | 4.350 | 1.470 | N.D | N.D |
| **Apricot** | 45.000 | 870.000 | 44.000 | 39.570 | 1.730 | 0.770 | N.D | 0.670 | 2.300 | 1.560 | N.D | 0.140 |
| **Orange** | 53.000 | 1791.700 | 88.600 | 128.400 | 0.050 | 0.400 | N.D | 0.630 | 3.920 | 1.620 | N.D | N.D |

## 3.5. Determination of Fluoride Content in Date

Fluoride content was determined in one of the most common type of dates in UAE, which is Lulu. 106.878 gram of the paste date was weighed and infused in 500 ml of deionized water, blended and stayed to brew for about 20 hours. 20 ml of the filtrate solution was mixed with the same volume of TISAB II and subjected to the FISE. The average value of the three replicate measurement of $F^-$ content in the date sample was 0.1146 mg/kg in dry matter. Also, the $F^-$ content of the date sample was determined from the acid digested sample using FISE after dilution and adjustment of the pH at 6.1 value. The acid digestion technique indicate that the $F^-$ content in Lulu date was 0.147 mg/kg of dry matter. The difference between the values obtained by the acid digestion and the infusion technique may be due to the complexation of $F^-$ with some metal ion in date sample. The inorganic $F^-$ complexes are not decomposed by infusion technique. Some types of organic and inorganic $F^-$ compounds (complexes) are difficult to release fluoride ion freely by infusion. Also, some silicate $F^-$ compounds are stable against even the acid digestion technique to release $F^-$ freely.

Many trials were applied using the IC technique for the infused date solution and results of calculated $F^-$ obtained were very high which is probably not corresponding to $F^-$ amount only but $F^-$ and other overlapped organic anion which both appeared at the same $F^-$ retention time and shows one peak (Fig. 3.36). This behaviour was observed during determination of $F^-$ in infused tea and in honey solutions using IC.

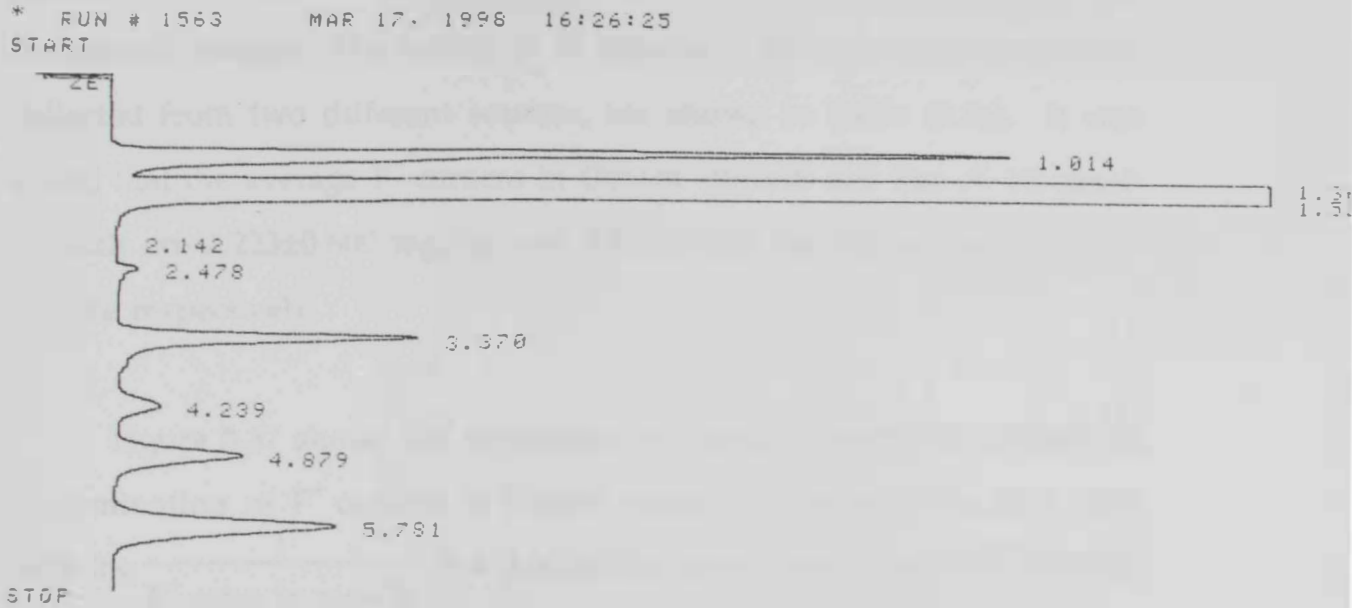


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Fig. 3.36. IC chromatogram for infused date solution of (70 gm in 500 ml deionized water stayed for 20 hours) followed by filtration and 5-fold dilution.

## 3.6. Determination of Fluoride in Spinach

According to the established technique for $F^-$ determination in plant tissue (ASTM, 1991), the fluoride content in the two samples of spinach was determined. The pH of the acidic sample solution was adjusted at 6 by mixing with TISAB II buffer solution. The latter mixed solution was subjected to FISE to measure the $F^-$ concentration level in the spinach sample. The results of $F^-$ content in the two spinach samples, collected from two different sources, are shown in Table (3.16). It was found that the average $F^-$ content in Omani spinach and Ras Al-Khiamah spinach are 2.223±0.600 mg/kg and 0.608±0.080 mg/kg of the dry plant sample respectively.

Figure 3.37 shows the application of standard addition method for determination of $F^-$ content in Omani spinach. The variation of E (mv) with $\log \frac{1}{F^- \text{ conc. in mol/L}}$ is a descending linear curve and the $F^-$ content in the investigated sample was found to be 2.578 mg/kg. However, the direct reading of $F^-$ content in the same sample is 2.7572 mg/kg.

The cationic content (mg/kg) of the investigated samples was measured from the ashed samples using ICP-ES (Table 3.16). It is well known that spinach plant tissue is rich of cation content (Table 3.16) and the highly content $F^-$ sample is the more rich in cations. Omani sample contains relatively high concentration levels of $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Al^{3+}$, $Mn^{2+}$ and the total Fe as well as the $F^-$ content. It should be mentioned that the ash percent of the spinach samples are 16.9% and 16.1% from the plant sample of the Omani and Ras Al-Khaimah samples.

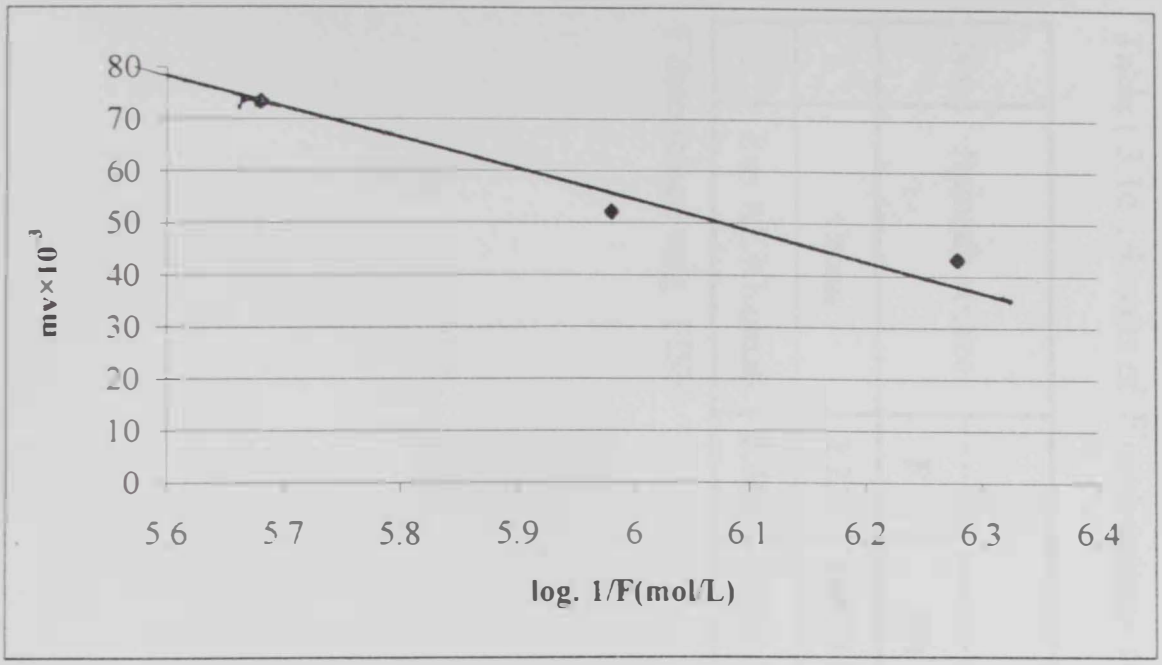



**Fig.3.37 Application of standard addition method for $F^-$ determination in Omani spinach sample .**

Table ( 3.16 ).Results of $F^-$ and cations analysis in the different sources of spinach samples using ICP.

| No. | Spinach source | Conc. mg /kg | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $F^-$ | $Na^+$ | $K^+$ | $Ca^{++}$ | $Mg^{++}$ | Total Fe | $Al^{+3}$ | $Mn^{++}$ |
| 1 | Oman | **2.223** | 16874.000 | 30996.000 | 15054.000 | 18516.000 | 88.870 | 114.200 | 53.870 |
| 2 | Ras AL Khaimah | **0.608** | 24841.000 | 19559.000 | 12480.000 | 11222 000 | 19.000 | 54.700 | 17.000 |

$F^-$determined usig FISE

## 3.7. Determination of Fluoride Content in Hamour Fish Samples

The acid digested solution of hamour fish samples was diluted with deionized water and the pH of the solutions was adjusted at pH 5.3 using NaOH solution followed by 15% $CH_3COONa$ (experimental part page 51). 20 ml of the latter solution was mixed with 20 ml of TISAB (II) buffer solution and subjected to $F^-$ analysis using a calibrated FISE. The $F^-$ content in the two samples having a different weight was found to be 0.9938 mg/kg and 0.8352 mg/kg of dry fish tissues for sample (I) and sample (II), respectively. The $F^-$ content in the two samples are more or less the same indicating that the age of fish does not affect the accumulation of $F^-$ in the fish tissue. It was found that the moisture content of the 1.5189 kg and 1.2432 kg weights of hamour fish samples are 73.76% and 76.63% respectively. The calculated $F^-$ content in whole fresh fish tissues (wet tissues) are 0.261 mg/kg for sample (I) and 0.1952 mg/kg for sample (II).

Fluoride ion content was measured from the infused solutions of both hamour fish samples, that is about 2 grams from the dried powdered fish tissues were mixed with 50 ml of boiling deionized water, allowed to stay overnight followed by filtration. The average fluoride ion content was taken for each sample as well as the blank. It was found that the $F^-$ content was 0.277 mg/kg of dry matter (0.0727 mg/kg of wet tissues) for sample (I) and 0.3696 mg/kg of dry matter (0.0864 mg/kg of wet tissues) for sample (II).

It can be noticed that the $F^-$ content measured from the infused tissues of both fish weights sample's solutions is lower than what have been obtained from the acid digestion technique. The difference between the results may due to the complexation of $F^-$ with some metal ions in fish sample as well as what have been interpreted for date sample (section 3.5).

Moreover, the cationic content of the two samples are more or less the same (Table 3.17). This table shows the fish samples are rich in $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$ and P whereas the concentrations of $Zn^{2+}$ and the total iron are relatively low. $Al^{3+}$ and $Mn^{2+}$ which are the commonly $F^-$ complexing metal ions are not detected. It can be concluded that the hamour fish could be considered as a moderate source of $F^-$ uptake.

**Table ( 3.17 ).Results of $F^-$ and cations analysis in the different weights of hamour fish samples using ICP.**

| No. | fish weight(kg) | Conc. mg /kg | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $F^-$ | $Na^+$ | $K^+$ | $Ca^{++}$ | $Mg^{++}$ | Total Fe | $Al^{+++}$ | p | $Zn^{++}$ | $Mn^{++}$ |
| 1 | 1.5189 | **0.994** | 992.500 | 13198.000 | 463.000 | 1254.000 | 7.588 | N D | 8466.200 | 11.380 | N D |
| 2 | 1.2432 | **0.835** | 1201.000 | 12252.000 | 596.000 | 1258.500 | 7.800 | N.D | 9412.000 | 11.920 | N D |

F determined usig FISE

# CHAPTER IV

## Part II

# Spectrophotometric Dtermination of Fluoride Ion

## 4.1. Introduction

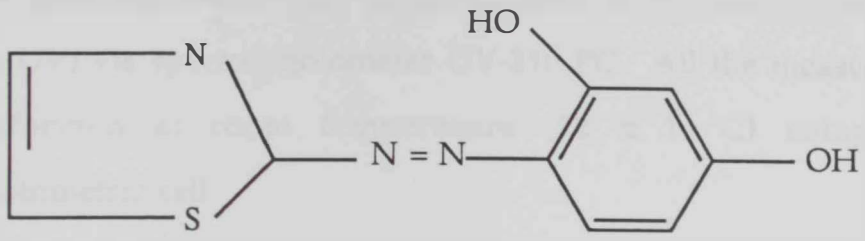
Numerous spectrophotometric methods for $F^-$ determination have been reported and can be classified into three groups: (i) substitution of the colored complexes with $F^-$ e.g. Zr(Ir)-solochrome cyanine R complex; (ii) catalytic action of $F^-$ on the complexation of polymeric hydrolyzed species e.g. Zr(IV)-xylenol orange and (iii) mixed ligand complex formation e.g. La(III)-Alizarine complexes. The method in group (i) was focused on the decrease in the absorbance of the metal ion complex and thus suffer from large blank absorbance. The method in group (ii) have a high sensitivity, but lacks reproducibility because of the difficulty in controlling the degree of hydrolysis of the metal ions. In these respects, the methods in group (iii) are superior, but there are only a few reaction systems and organic reagents are always used for $F^-$ determination. The most widely used for application of the (iii) method are the La, Zr, Th, Ce and Al complexes of Alizarine and pyridyl-azo-naphthol (PAN). It should be mentioned that most of these complexes have the drawback of slow reaction rates in aqueous solutions (Yuchi, A. and others, 1993).

The present work includes the determination of $F^-$ spectrophotometrically using Zr(IV)-Thiaazolyl-azo-resorcinol (TAR) complex. A colored development mechanism due to formation of Zr-TAR-F mixed complex was considered. The optimum conditions for $F^-$ determination and the straight line calibration curve method were reported. Also, development of the method for determination of $F^-$ in real sample e.g. mouth wash solution was reported.

## 4.2. Experimental

### 4.2.1. Reagents and Solutions:

4-(2-Thiazolylazo)-resorcinol (TAR) reagent has been obtained through Aldrich chemicals company and have been used without further purifications. The structure of the TAR reagent is represented as follows:




Structure of TAR reagent

Sodium fluoride was dried in a crucible for 2.4 hour at 100 °C. $1x10^{-3}$ mol/L solution of $F^-$ was prepared in deionized water and the working solutions were prepared by diluting the appropriate volume using deionized water.

0.05 mol/L sodium acetate solution containing 0.05 mol/L KCl (KCl was added to keep the ionic strength of solution) was used as a buffer solution the desired pH solutions were prepared using acetic acid and NaOH solutions. Stock solutions of the metal cations and anions solutions were prepared and the dilute concentration solutions were prepared using deionized water. All other reagents used were of analytical grade (BDH).

A Zr(IV) stock solution ($1x10^{-3}$ mol/L) was prepared by dissolving an appropriate weight of $Zr(SO_4)_2$ in deionized water in presence of few drops of

concentrated $H_2SO_4$, which prevents the formation of polymeric hydrolyzed species. Also, the dilute solutions were prepared by diluting of the stock solution with deionized water.

### 4.2.2. Instrumentation:

The spectrophotometric measurements were carried out using Shimadzu UV/Vis spectrophotometer UV-210 PC. All the measurements were performed at room temperature (22 ± 1 °C) using 1 cm spectrophotometric cell.

The pH of the solutions was adjusted using Metrohm pH-meter, Model 691.

## 4.3. Spectrophotometric Behaviour of TAR and its Zr(IV) Complexes

The general spectrophotometric behaviour of TAR and its acid/base equilibria had been previously established (Cheng and Others, 1982) and could be represented as follows;

$$H_3L^+ \xrightleftharpoons{pK_a\ 0.96} H_2L \xrightleftharpoons{pK_b\ 6.3} HL^- \xrightleftharpoons{pK_b\ 9.3} L^{2-}$$

| | | | | |
|---|---|---|---|---|
| $\lambda_{max}$ | 384 | 439 | 481 | 510 |
| $\epsilon_{max}$ | $2.9\times10^4$ | $2\times10^4$ | $2.9\times10^4$ | $3.45\times10^4$ |

in water/dioxane mixture

The object of the work is the determination of $F^-$ in aqueous or aqueous-ethanol mixture using Zr(IV)-TAR reagent. Therefore, the spectral behaviour of TAR and Zr(IV)-TAR complexes in aqueous-ethanol was examined over 300-700 nm wavelength in solutions of varying pH (Fig's 4.1, 4.2 and 4.3). The spectral behaviour of TAR characterizes with a broad spectral peak centered at 430-485 nm (pH dependent). In acid solutions (pH $\leq$ 5), in presence of equimolar concentration of Zr(IV) or higher, using TAR reagent as a blank solution, the TAR peak completely disappear (Fig's 4.1 and 4.2) and a new peak was observed at 540 nm. The latter peak corresponding to the Zr(IV)-TAR complex, which formed between Zr(IV) and the neutral form of TAR. In neutral and alkaline solutions (pH $\geq$ 6.0) and in presence of excess molar concentration of Zr(IV) e.g. TAR-Zr(IV) 1:20 using TAR as a blank the Zr(IV) complexes of TAR shows two spectral peaks at 460 and 540 nm (Fig. 4.3). It should be

mentioned that the longer wavelength peak recorded as a shoulder in presence of relative low concentration of Zr(IV).

In acidic media, the intensity of Zr(IV)-TAR complex peak enhanced in presence of $F^-$ and its molar absorptivity increases markedly (Fig's 4.1, 4.2) with increasing $F^-$ concentration. In neutral and alkaline media ($6.0 \leq pH \leq 9.0$) the intensity of the longer wavelength peak of the anionic TAR-Zr(IV) complex enhanced and its absorption increases clearly with increasing $F^-$ concentrations (Fig. 4.3). The shorter wavelength peak of the anionic TAR-Zr(IV) complex decreases to some extent with increasing $F^-$ concentrations. This behaviour could be explained by the formation of the ion associated form between the positively charged species $[Zr(HL)_2]^{2+}$ of Zr-TAR complexes and negatively charged $F^-$, since there is no change in the peak position of Zr(IV) complex upon addition of $F^-$.

It is worthy of mentioning that due to the hydrolysis of Zr(IV) in strong alkaline solutions ($pH \geq 9.0$) there is no spectral evidence for the formation between Zr-TAR and/or Zr-TAR-$F^-$.

## 4.4. Spectrophotometric Determination of Fluoride Ion Using Zr(IV)-TAR Complex

In order to obtain the optimum conditions for $F^-$ determination using Zr(IV)-TAR complex, the effects of pH, ethanol percentage, Zr(IV)/TAR ratio, time and the interfering anions and cations on the spectral behaviour of Zr(IV)-TAR-$F^-$ system were considered. The effect of pH on the absorbance of the Zr(IV)-TAR-$F^-$ system was investigated at 2.3-9.9 pH range. Fig. 4.5 shows the increases in the absorbance (the difference between the absorbance of Zr(IV)-TAR and Zr(IV)-TAR-$F^-$ complexes) - pH plot, the difference in the absorbance increases gradually with increasing the pH and the maximum increment in the absorbance was found at pH 7.30. Therefore, the pH 7.3 was chosen for the analytical determination of $F^-$ using Zr(IV)-TAR complex.

The effect of ethanol percentage on the absorbance of the Zr(IV)-TAR-$F^-$ system was checked and represented in Fig. 4.6. It was found that with increasing the percentage of ethanol the intensity of the peak increases till 20% (v/v) ethanol buffer mixture and becomes constant at higher ethanol percentage. This result indicate that 20% ethanol is suitable for maximum solubility of the system. The time dependency of the investigated system (Zr(IV)-TAR-$F^-$) was considered at pH 7.3 and in presence of 20% ethanol. It was found that the system as well its spectral behaviour is stable between 2-5 hours.

At pH 7.3 in buffer solution containing 20% ethanol the effect of $F^-$ concentration on the spectral behaviour of Zr(IV)-TAR-$F^-$ was

investigated (Fig. 4.7). The shorter wavelength peak decreases gradually with increasing the $F^-$ concentration indicating that the original Zr(IV)-TAR species decomposes gradually. However, the longer wavelength peak at 540 nm increases gradually with increasing $F^-$ concentration. Beer's law was applied on the variation of the absorbance of the longer wavelength peak with $F^-$ concentration over a $1x10^{-5}$ - $5x10^{-5}$ mol/L $F^-$ concentration range. A calibration curve straight line was obtained passes the origin with a correlation coefficient of the fit (r) equals 0.9931 (the first three points on the straight line was considered on calculations) and relative standard division of the fit was found to be 0.146. The detection limit of $F^-$ was calculated from the 3 times of the signal/noise ratio and it was found to be $1.364 \times 10^{-5}$ mol/L (0.258 mg/L).

The aim of this work is the application of the above method for $F^-$ determination in some real samples that contain $F^-$ e.g. mouth wash solution. Therefore, the interfering effects of some cations and anions on the spectral behaviour of Zr(IV)-TAR-$F^-$ system were considered. The effects of $1x10^{-5}$ mol/L of $Al^{3+}$, $Fe^{3+}$, $Cu^{2+}$, $Zn^{2+}$, $Ca^{2+}$ and $Mg^{2+}$ on the spectral behaviour of the investigated system was studied (Fig's 4.9, 4.10). There is no marked change is seen in the spectral behaviour of the system in presence of $Al^{3+}$, $Fe^{3+}$, $Cu^{2+}$, $Ca^{2+}$ and $Mg^{2+}$, however, in presence of $1x10^{-4}$ mol/L $Zn^{2+}$ the longer wavelength peak (analytical determination of $F^-$ peak) is almost duplicate (Fig. 4.10). This result indicates that the Zn(II)-TAR complex has a spectral peak that is completely overlapping with the spectral peaks of Zr(IV)-TAR-$F^-$ system. Also, it indicates that the determination of $F^-$ in presence of Zn(II) using this system is impossible.

Fig. 4.11 shows the interfering effects of $1x10^{-4}$ mol/L of $HCO_3^-$, $Cl^-$, $SO_4^{2-}$, $CO_3^{2-}$ and $PO_4^{3-}$ on the analytical determination peak of $F^-$ using Zr(IV)-TAR-$F^-$ system. $Cl^-$, $SO_4^{2-}$, $PO_4^{3-}$ have no interfering effect on the spectral behaviour of the investigated system, however, $HCO_3^-$ and $CO_3^{2-}$ slightly affect the intensity of the $F^-$ analytical determination peak (the longer wavelength peak of the investigated system).

## 4.5. Determination of $F^-$ Content in Mouth Wash

The application of Zr(IV)-TAR system as spectrophotometric reagent for $F^-$ determination was investigated at pH 7.25. 10 mL of the mouth wash solution were transferred into 50 mL measuring flask and diluted to the mark using bi-distilled water. 3.5 mL of the latter solution was mixed with 1 mL of $5x10^{-4}$ mol/L Zr(IV) and 1 mL of $1x10^{-4}$ mol/L TAR in 10 mL measuring flask and completed to the mark using sodium acetate and potassium chloride solution (0.05 M KCl and pH 7.25). The spectrum of this solution was measured over 300-600 nm wavelength range using $1x10^{-5}$ mol/L TAR as a blank. The absorbance at 540 nm was measured and the $F^-$ content in the solution was calculated using the calibration curve method. It was found that the $F^-$ content in the mouth wash sample is 1.979 mg/10 mL. The degree of recovery of the $F^-$ content in the mouth wash sample according to the listed value on its chemical composition label is 98.300%. Table 4.1 recorded the degree of recoveries calculated for the F- content in the commercial mouth wash sample according to chemical composition label of the product.

Table 4.1. Degree of recoveries of the F- content in the commercial mouth wash product using the various analytical methods of analysis.

| Method | $F^-$ content mg/10 mL | | |
|---|---|---|---|
| | Listed | Found | Recovery |
| Spectrophotometric | 2.014 | 1.979 | 98.300 |
| FISE | 2.014 | 2.168 | 107.646 |
| IC | 2.014 | 2.009 | 99.751 |

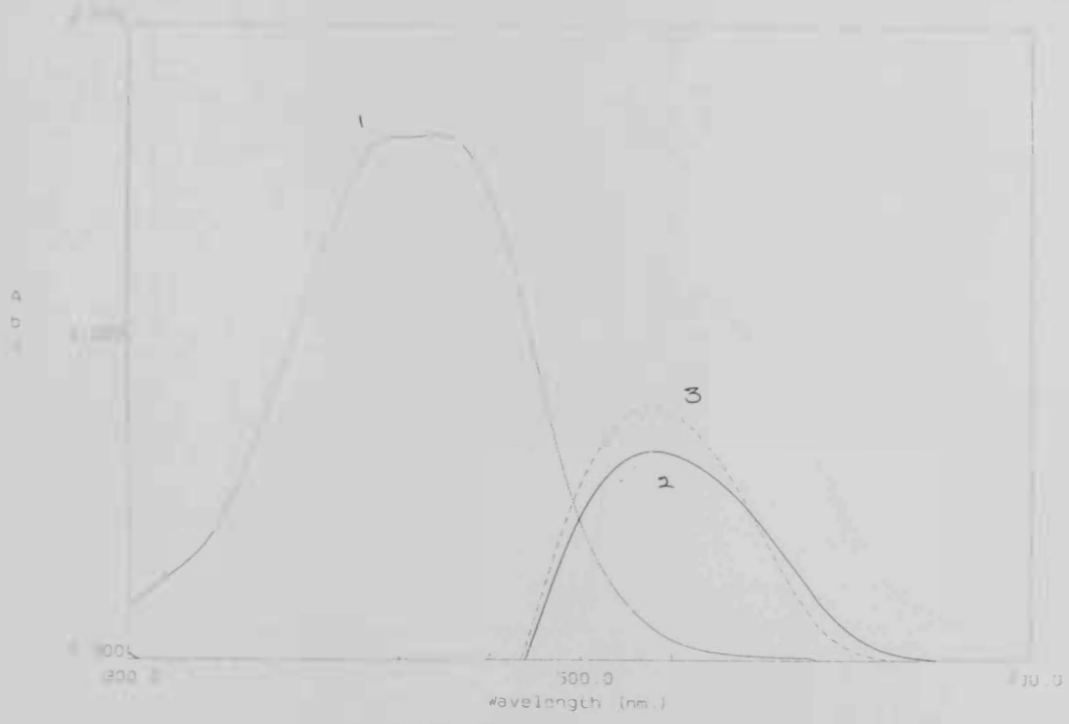



Fig. 4.1. Absorption spectra of (1) $1x10^{-5}$ mol/L TAR, (2) $1x10^{-5}$ mol/L TAR + $5x10^{-5}$ mol/L Zr(IV) and (3) 3 + $1x10^{-5}$ mol/L $F^-$ at pH 2.3.

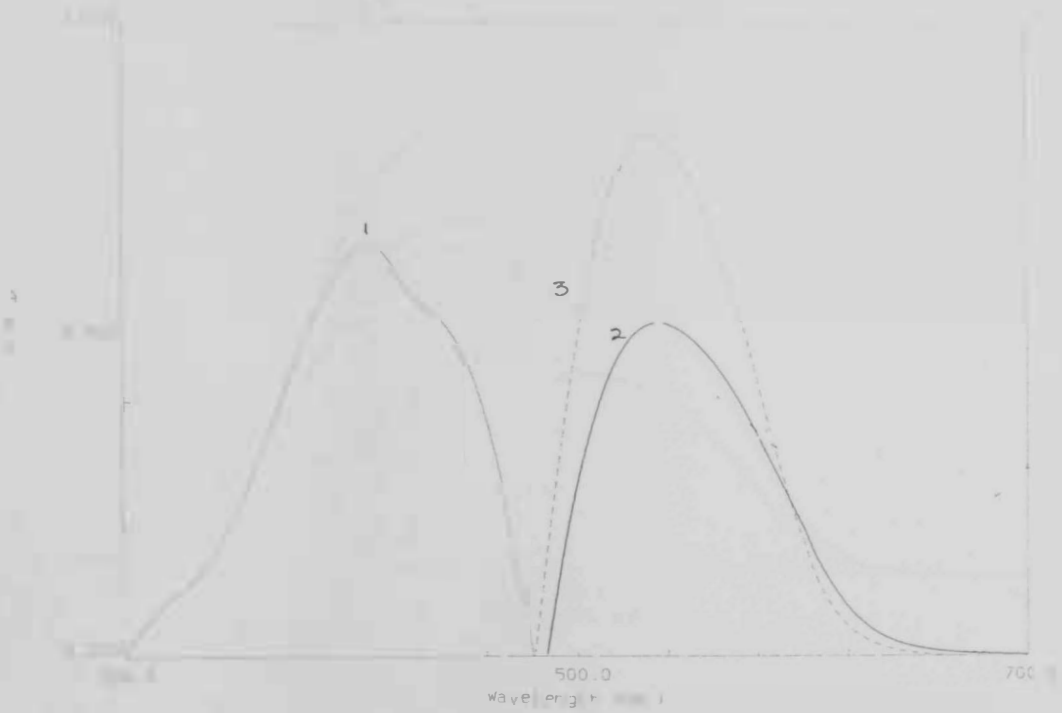



Fig. 4.2. Absorption spectra of (1) $1x10^{-5}$ mol/L TAR, (2) $1x10^{-5}$ mol/L TAR + $5x10^{-5}$ mol/L Zr(IV) and (3) 3 + $1x10^{-5}$ mol/L $F^-$ at pH 5.3.

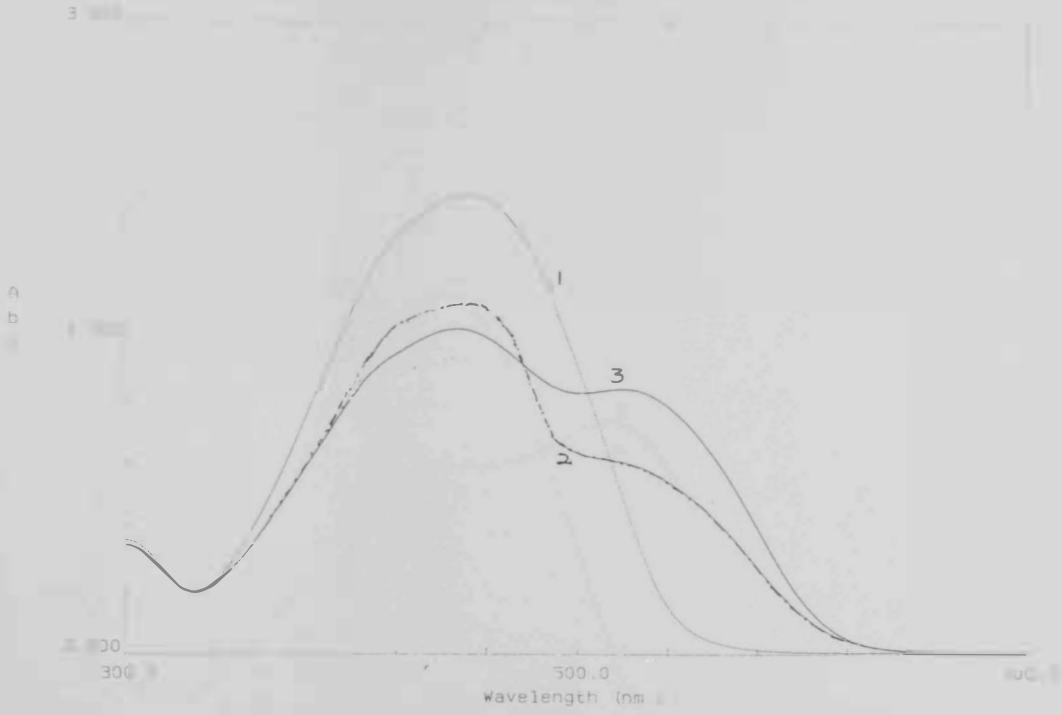



Fig. 4.3. Absorption spectra of (1) $1x10^{-5}$ mol/L TAR, (2) $1x10^{-5}$ mol/L TAR + $5x10^{-5}$ mol/L Zr(IV) and (3) 3 + $1x10^{-5}$ mol/L $F^-$ at pH 7.25.

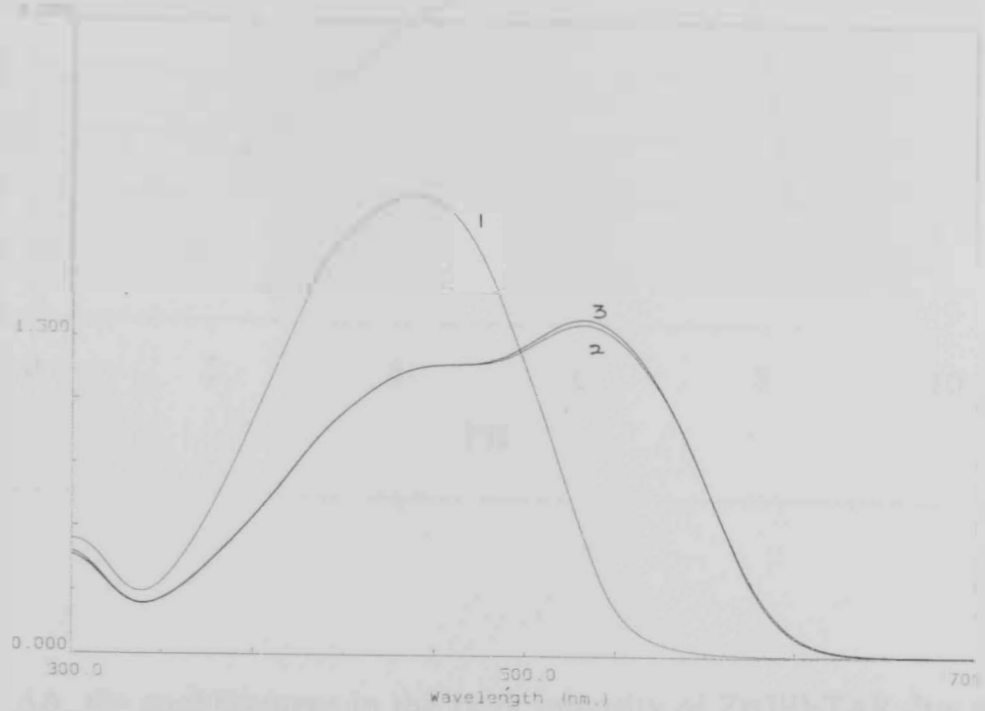



Fig. 4.4. Absorption spectra of (1) $1x10^{-5}$ mol/L TAR, (2) $1x10^{-5}$ mol/L TAR + $5x10^{-5}$ mol/L Zr(IV) and (3) 3 + $1x10^{-5}$ mol/L $F^-$ at pH 8.3.

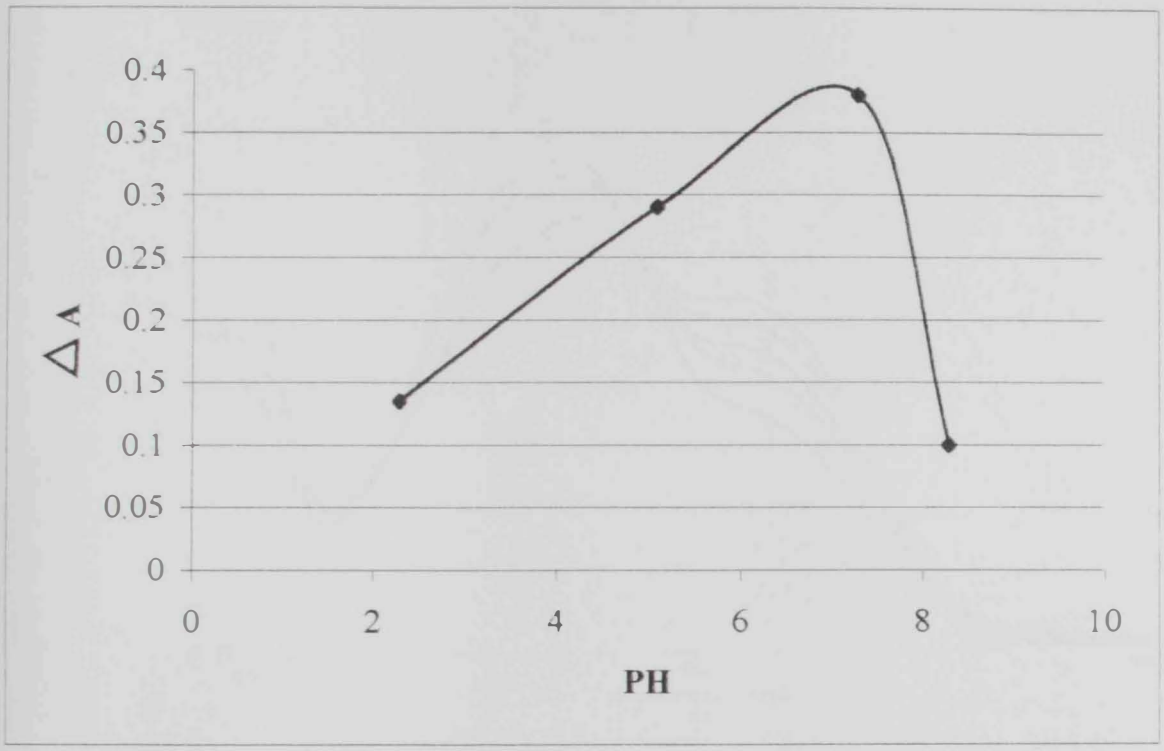



Fig. 4.5. ΔA, the enahncement in the peak intensity of Zr(IV)-TAR due to addition of $F^-$ against pH-plot.

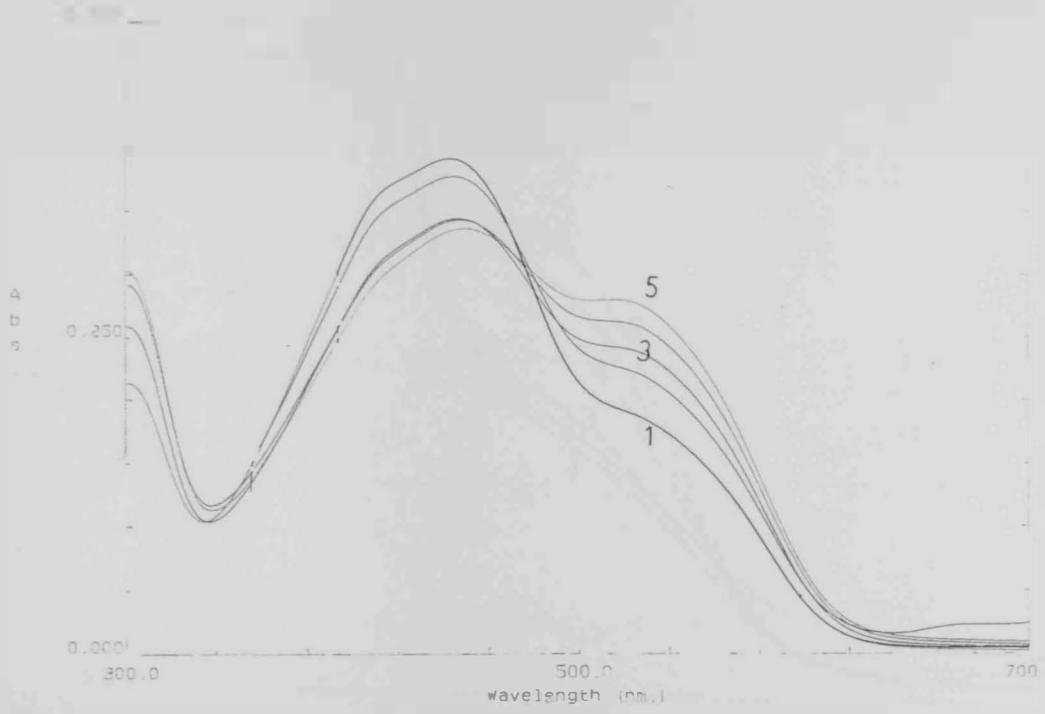



Fig. 4.6. Effect of ethanol percentage on the absorption spectra of $1x10^{-5}$ mol/L TAR + $5x10^{-5}$ mol/L Zr(IV) and $3x10^{-5}$ mol/L $F^-$ at pH 7.3.

(1) 0.0 , (2) 5.0 , (3) 10.0 , (4) 15.0 and (5) 20% ethanol.

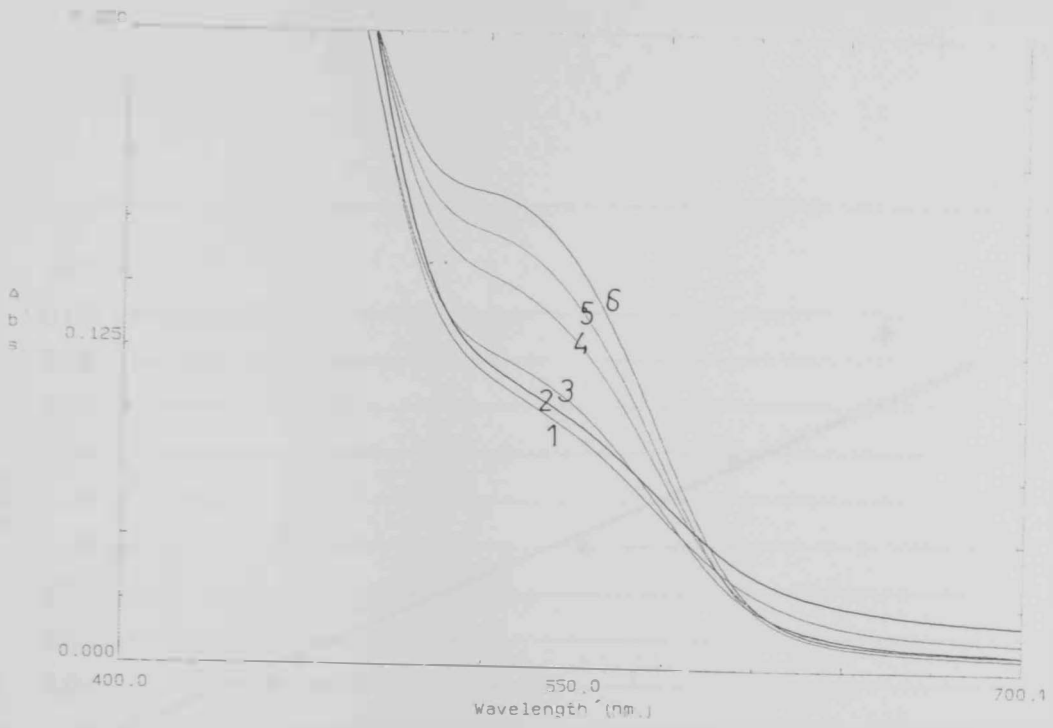



Fig. 4.7. The absorption spectra of Zr(IV)-TAR system in the presence of various $F^-$ concentration at pH 7.3 in presence of 20% ethanol. (1) 0.0 , (2) $1x10^{-5}$ , (3) $2.5x10^{-5}$ , (4) $3.0x10^{-5}$ , (5) $4x10^{-5}$ and (6) $5x10^{-5}$ mol/L $F^-$.

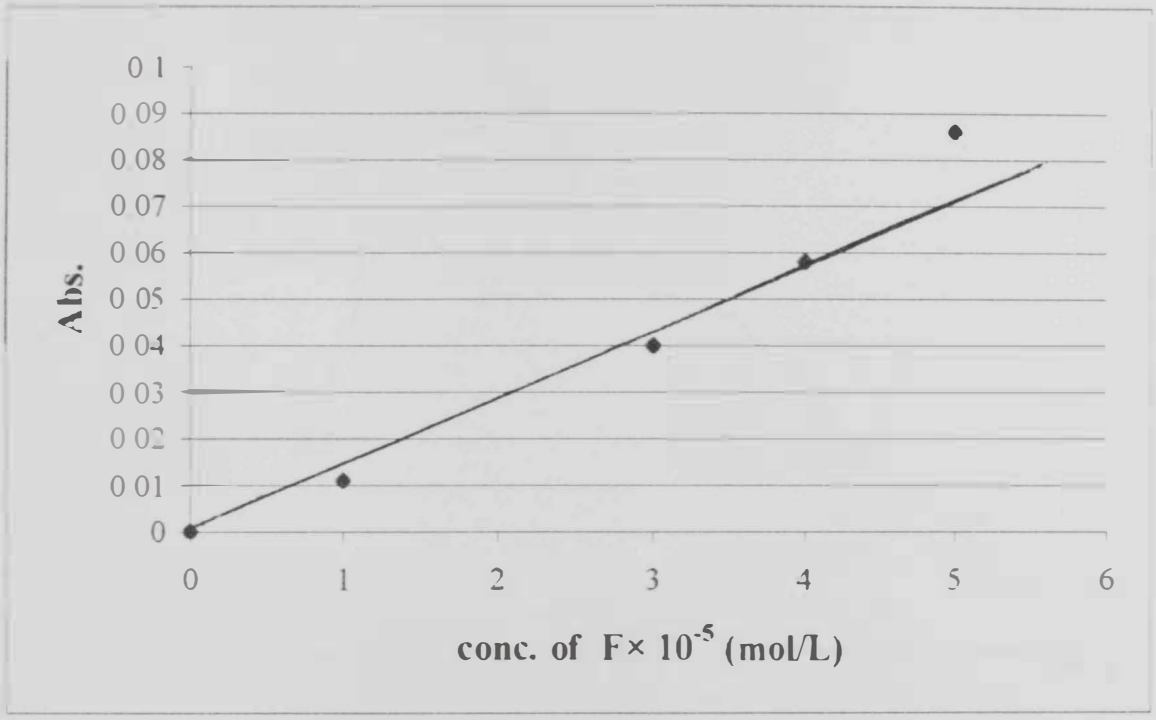



Fig. 4.8. Straight line calibration curve for $F^-$ determination using Zr(IV)-TAR system at pH 7.25.

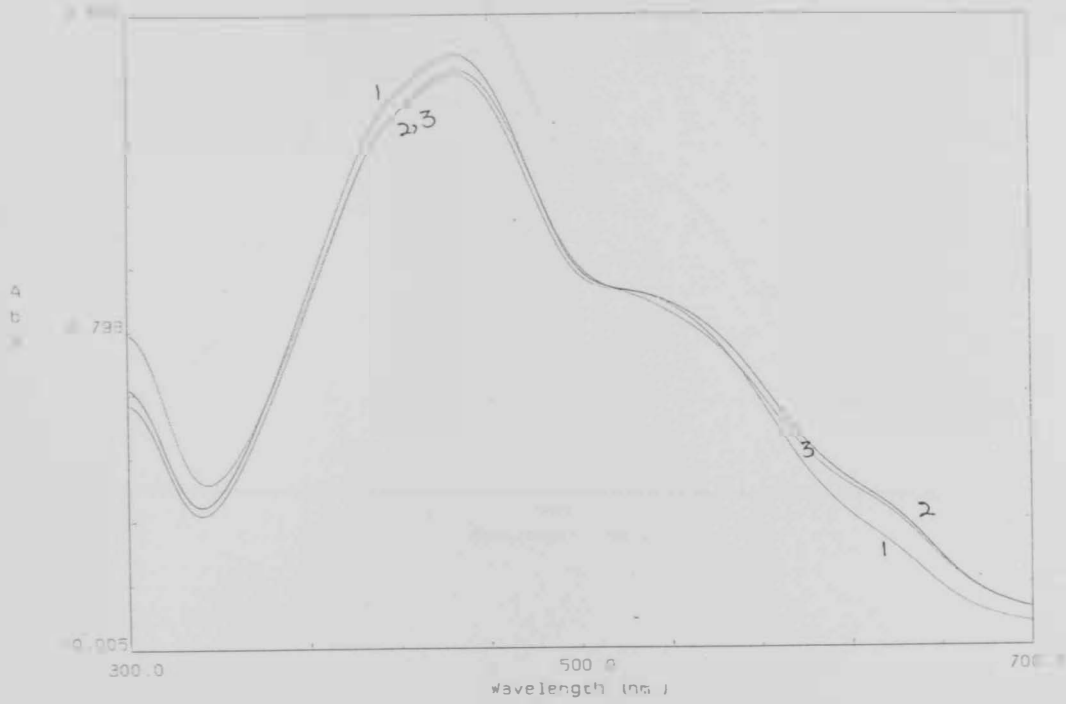



Fig. 4.9. Absorption spectra of (1) Zr(IV) + TAR + $F^-$ system in the presence of (2) $1x10^{-4}$ mol/L $Al^{3+}$ and (3) $1x10^{-4}$ mol/L $Fe^{3+}$ at pH 7.25.

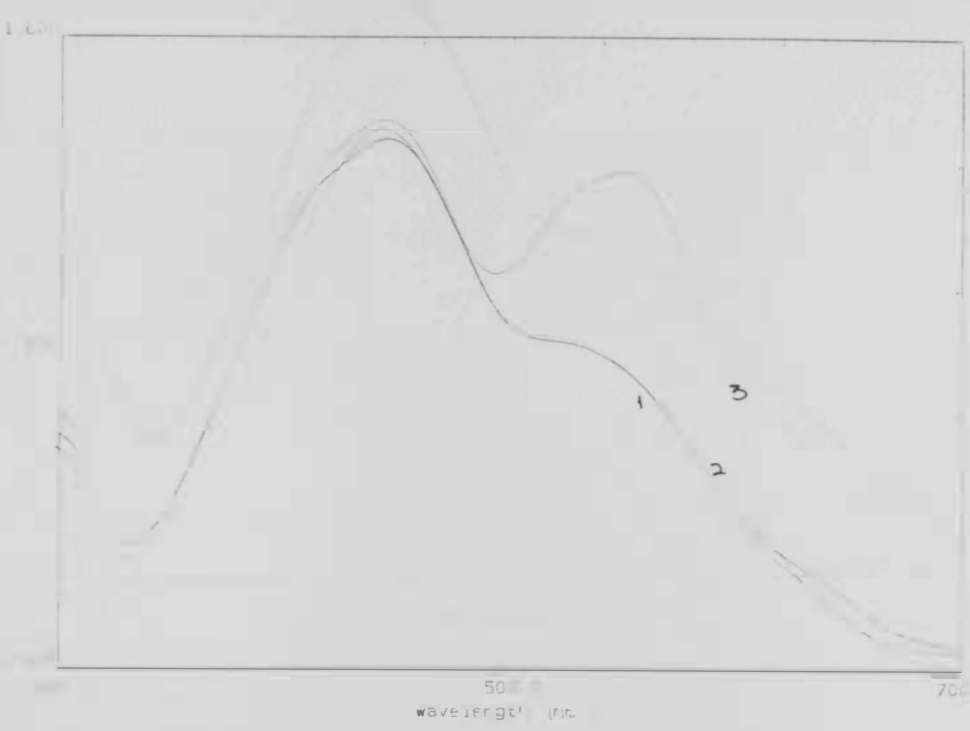



Fig. 4.10. Absorption spectra of (1) Zr(IV) + TAR + $F^-$ system in the presence of (2) $1x10^{-4}$ mol/L $Cu^{2+}$ and (3) $1x10^{-4}$ mol/L $Zn^{2+}$.

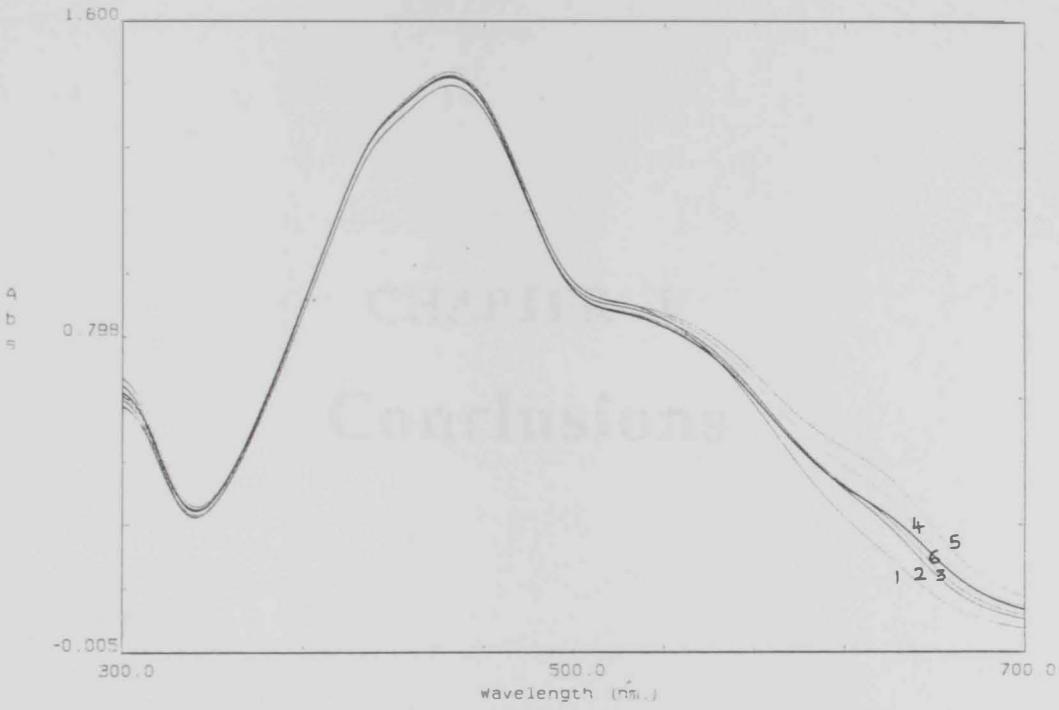



Fig. 4.11. Absorption spectra of (1) Zr(IV) + TAR + $F^-$ system in the presence of $1x10^{-4}$ mol/L of (2) $HCO_3^-$, (3) $Cl^-$, (4) $SO_4^{2-}$, (5) $CO_3^{2-}$ and (6) $PO_4^{3-}$.

# CHAPTER V

# Conclusions

# CONCLUSIONS

The objectives of the present study were to study the fluoride content in drinking water and some foods consumed in the U.A.E. in order to draw basic data for fluoride intake.

The present study also was initiated to incorporate an earlier study and surveillance programme by the Ministry of Health about the status of dental caries in the U.A.E. The survey concluded that there were high levels of dental caries among children (aged 6-12 years) in urbanized areas, and relatively lower percentages in rural and geographically isolated places.

In the U.A.E. there has been no monitoring for the sources of fluoride exposure yet. As there is more change to desalinated water, less exposure from drinking water will occur and less fluorosis will be observed in children. However, in the Ministry of Health consultancy services, it was decided that more information is required to cover the following:

1. A nationwide evaluation and regular monitoring of fluoride level in drinking water.

2. A comprehensive oral epidemiologic survey of child and adult population.

3. An evaluation of the socio-cultural determinants of fluoride exposure and

4. An assessment of additional sources of fluoride exposure, e.g., food and beverages, dental products.

Once such data are available, formal decisions regarding protective programs including water fluoridation can be made.

In our opinion items No. 1 and 4 are the most prominant and effective parameters in the present study which concentrate on fluoride presence in water and food.

Regarding the above, it must be born in mind that:

1. Though fluoride is not conclusively proved to be an essential nutrient for human consumption, several studies have shown that fluoridation of drinking water helps reduced dental caries incidences especially among children and that

2. Improvement in dental health due to fluoridation, however, is only partial, i.e., only 40-60% lower incidence of dental canes were noticed among population drinking fluoridated water in comparison with those consuming non-fluoridated water.

The present study has shown that the fluoride content in drinking water (desalinated water which is tap water), bottled water, underground water and some food items in Abu Dhabi local markets and the results are summarized in Table 5.1.

Table 5.1. Results of determination of $F^-$ in various water and food samples.

| Food | $F^-$ Content | | |
|---|---|---|---|
| | Minimum | Maximum | Average |
| Bottled water | B.D.L.* | 0.35 mg/L | 0.103 mg/L |
| Desalinated water (tap water) | ------ | B.D.L.* | ------ |
| Well water (Liwa) | 1.5 mg/L | 5.7 mg/L | 3.828 mg/L |
| Holy Zamzam water | ------ | ------ | 0.398 mg/L |
| Tea | Al-Wazza = 0.914 mg/L or 0.091 mg/tea bag | Lipton = 4.3 mg/L or 0.428 mg/tea bag | 2.33 mg/L |
| Honey | Sudani = B.D.L. | Yemeni = 0.597 mg/Kg | 0.314 mg/kg |
| Commercial fruit juice | Orange = 0.02 mg/L | Grape = 0.17 mg/L | 0.07809 mg/L |
| Lulu date | ------ | ------ | 0.147 mg/kg |
| Spinach | Ras Al-Khaimah = 0.603 mg/kg dry weight | Omani = 2.223 mg/kg dry weight | 1.4155 mg/kg dry weight |
| Hamour fish | 0.1952 mg/kg wet tissues | 0.261 mg/kg wet tissues | 0.2281 mg/kg wet tissues |

* B.D.L. = Below detection limit.

The amount of $F^-$ found in water and food samples in the present study shows that the drinking water is inadequate as a source of fluoride intake particularly in cities like Abu Dhabi. The intake is almost zero, while the intake in rural areas when well water is consumed seemed adequate.

The intake of fluoride from food seemed sufficient especially from tea and sea food. The uptake from tea is 1.17 mg/day and from fish is approximately 0.034 mg/day. However, the uptake from other sources was small like vegetables (spinach) 0.22 mg/day, fruit juices 0.02 mg/day and dates 0.015 mg/day. The total uptake of $F^-$ from food items studied is approximately 1.5 mg/day.

From the above it can be safely concluded that the uptake of fluoride from food in the UAE is almost adequate but from water is deficient. We have to bear in mind that this uptake is by the adult population only.

For children aged 6-12 years who do not drink tea in appreciable amounts, there seems to be deficiency in their fluoride uptake since the water is the more appropriate uptake route for them. The following recommendation can be made regarding drinking water for children either the community water can be fluoridated or at least bottled water intended for their use can be fluoridated, taken into consideration the climatic conditions. Desalinated water should be fluoridated that is due to the substantial benefits obtained from fluoridation particularly in

preventing dental caries especially in children. If fluoridation of desalinated water is not feasible, then at least bottled water should be fluoridated to enhance the fluoride intake in children diet who normally do not consume large amounts of tea or fish. However, the fluoride intake by adults can be found by consumption of tea and fish which are widely consumed in the Gulf area.

Another prospect of this study is the development of a spectrophotometric method for fluoride ion determination in some samples. In this context, Zr(IV)-thiazolylazo rezorcinol system was used as an analytical reagent for $F^-$ determination. The Zr(IV)-TAR complex was characterized by a maximum absorption peak at 460 nm and a shoulder at 540 nm. The latter shoulder was developed in presence of $F^-$ showing a well developed peak, whereas the peak at 460 nm was decreased. The absorbance of the peak at 540 nm is varied linearly with the concentration of $F^-$ within the range of concentration of 0.19-0.95 mg/L and the detection limit was found to be 0.258 mg/L. The developed method was used for the determination of $F^-$ in mouth wash. The degree of recovery of $F^-$ as compared to the reported value of the chemical composition label was 98.3%. Moreover, comparison of the degree of recovery of $F^-$ in mouth wash as calculated by the spectrophotometric method, IC and FISE measurements was in the range 99.8-107.6%.

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# ARABIC SUMMARY

بلغ معدل محتوى الفلورايد في عينات الشاي موضوع الدراسة حوالي ٢،٣٣ ملجم/لتر وبذلك يعتبر الشاي مصدر طبيعي جيد للفلورايد.

ويعد السبانخ وسمك الهامور من المصادر المعتدلة في محتواها من الفلورايد بينما نجد أن كل من العسل والعصائر والتمر (موضوع الدراسة) تحتوي كميات ضئيلة من الفلورايد.

كما يشمل الفصل الرابع وصف لتطبيق الطرق الطيفية في تقدير أيون الفلورايد في عينات تجارية، إذ تعتمد هذه الطريقة على استخدام جوهر من مادة زيركونيوم - ثيازولايل آزو ريزورسينول (تار).

لقد أظهرت النتائج أن الحد الأدنى لتقدير الفلورايد بهذه الطريقة بلغ $١٠x١^{-٥}$ مول/لتر.

تم تطوير هذه الطريقة لتقدير الفلورايد في محاليل غسل الفم التجارية وقد وجدت نتائج التحاليل مطابقة لما صرح به في البطاقة الخاصة بالمحلول بنسبة ٩٨،٣٪.

وقد تناول الفصل الخامس تلخيص لنتائج تحاليل الفلورايد في العديد من عينات مياه الشرب المتنوعة والعينات الغذائية المختلفة بالإضافة إلى التوصيات التي أشارت إلى إمكانية فلورة مياه الشرب وعلى أقل تقدير مياه الشرب المعبأة لما لها من تأثيرات إيجابية في التقليل من تسوس الأسنان وخصوصاً لدى الأطفال. وقد جاءت هذه التوصيات كحل وسط لمعارضي فلورة المياه المحلاة والتي تستخدم لأغراض أخرى مختلفة غير الشرب منها الري وغيرها من الاستعمالات الخارجية للإنسان وبذلك فقد يشكل فلورتها هدراً اقتصادياً.

إذ أن فئات البالغين تحصل على حاجتها من الفلورايد من المواد الغذائية كالشاي والسمك التي قلما يتناوله الأطفال إلا في بعض الحالات والتي لا توفي بالمتطلبات اليومية من الفلورايد.

## الملخص العربي

في السنوات الأخيرة ولد وجود كميات الفلورايد في العينات البيولوجية، مياه الشرب، والمواد الغذائية أو الأعلاف الحيوانيه المحتوية على الفلورايد اهتماماً كبيراً. وبذلك بدأ تقدير نسب وكميات الفلورايد يحظى باهتمام متزايد نظراً لما له من آثار سلبية ضارة على صحة البيئة.

يعد الفلورايد من بين الملوثات الشديدة السمية على النباتات. وكنتيجة لذلك أجريت بحوث مكثفة لتحسين طرق تقدير الكميات الضئيلة أو الآثار الضئيلة من الفلورايد وذلك بتطوير الطرق التحليلية المختلفة وقد نالت تطبيقات هذه الطرق التحليلية للفلورايد في الماء والعينات الغذائية اهتماماً كبيراً.

يتضمن الفصل الأول من هذا البحث الخصائص الرئيسية للفلورايد من حيث توفره في البيئة، التأثيرات الفسيولوجية وميكانيكية عمله في التقليل من تسوس الأسنان. كما احتوى الفصل على حصر علمي للعديد من التطبيقات لطرق تحليل أيون الفلورايد في العديد من العينات البيئية.

كما يمثل الفصل الثاني الجزء العملي من هذه الأطروحة حيث يحتوي على وصف للكيماويات والمواد المستخدمة وطرق تحضير العينات المختلفة وطرق التحليل بالإضافة إلى الأجهزة المستخدمة في التحليل. كما يشمل هذا الفصل التقنيات والطرق العامة القياسية لتقدير أيون الفلورايد في العينات البيئية.

كما احتوى الفصل الثالث على نتائج تحاليل الفلورايد في عينات مياه مختلفة، شاي، عسل، عصائر، تمر، سبانخ وسمك الهامور وقد أظهرت النتائج أن معدل محتوى الفلورايد في المياه المعبأة حوالي ٠،١٠٣ ملجم/لتر والذي يعتبر أقل نسبياً من محتوى الفلورايد في مياه الآبار للمنطقة الغربية من امارة أبوظبي (ليوا).

كما أظهرت النتائج عدم احتواء المياه المحلاة على الفلورايد، في الوقت الذي احتوت فيه مياه زمزم المقدسة على ٠،٤ ملجم/لتر.

جامعة الإمارات العربية المتحدة

كليـــــــــة العلـــــــــوم

عنوان الرسالة : دراســـات حـــول وجـــود الفلوريد في بعض العينـــات الغذائيـــة

اسم الطالبة : تغريد على عبد الله الحبشي

## لجنة التحكيم

| الاسم | الوظيفة | التوقيع |
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**عنوان الرسالة : دراســات حــول وجــود الفلوريد في بعض العينــات الغذائيــة**

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## لجنة الإشراف

| الاســـــــــــم | الوظيفـــــــة | التوقيـــــع |
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جامعة الإمارات العربية المتحدة

كليـــــــــة العلـــــــــوم

# دراســـات حـــول وجـــود
# الفلوريد في بعض العينـــات الغذائيـــة

رسالة مقدمة من الطالبة

تغريد علي عبد الله الحبشي

بكالوريوس في العلوم (رئيسي: كيمياء / فرعي: بيولوجي)

استكمالا لمتطلبات الحصول على درجة الماجستير في العلوم

(علـــــــوم البيئـــــــة)

جامعة الإمارات العربية المتحدة

كليـــــة العلـــــوم

ديسمبر ١٩٩٨