STUDY OF COMMON INORGANIC ANIONS IN WATER SAMPLES OF QUETTA CITY BY TECHNIQUE OF ION CHROMATOGRAPHY

Manzoor Iqbal Khattak
Chemistry Department , Balochistan University, Quetta, Pakistan
manzoor_iqbal@yahoo.com

ABSTRACT: The major inorganic anions (fluoride, chloride, nitrate, and sulfate) in the water samples of Quetta were determined by Ion chromatography with suppressed conductivity detection. In the experiment, the eluent was 2.0 mmol/L Na_2CO_3 and 1.3 mmol/L $NaHCO_3$.The purpose of present work is to quantitatively assess and evaluate the anions F^-,Cl^-, NO_3^-, PO_4^{-3}, and SO_4^{-2} in potable water with a view to find ways and means to bring the minimum inorganic anions concentration of the drinking water in use of inhabitant of Quetta to at least the minimum WHO guideline value.

Key words: Inorganic anions, Ion chromatography, Suppressed conductivity detection, Water contamination, Drinking water, WHO guidelines.

1. INTRODUCTION

In district Quetta, the quality of ground water varies from place to place. In most of the places water is of good quality while in Balali, Mehtarzai, Samalani and Mallahzai the quality of water is very poor (saline / brackish) and not potable. The chemical quality of water can be established by chemical analysis. The World Health Organisation (W.H.O) have set some standard parameters such as the quantity of calcium, magnesium, sodium sulphate and nitrate etc., to differentiate potable water from non-potable.

Drinking water is derived from two basic services, surface water, such as rivers and reservoirs and ground water. All water contains natural contaminates that arises from the geological data through which the water flows and to a varying extent, anthropogenic pollution by both microorganisms and chemicals [1]. The level of water contaminant varies from region to region. The contamination of water is a direct reflection of the degree of contamination of the environment. After flushing air borne pollutants from the skies, rain water literally washed over the entire human landscape before running into the aquifers, streams, rivers, and lakes that supply our drinking water. Any and all of the chemicals generated by human activity can and will find there way into water supplies. Contaminations may also arise from the compounds contained in the pipes, fixtures of the water distribution system.

Many epidemiological studies of possible adverse effects of the long term ingestion of fluoride via drinking water have been carried out. High intakes of fluoride can give rise to dental fluorosis, an unsightly brown mottling of teeth, but higher intake result in skeletal fluorosis, a condition arising from increasing bone density and which can eventually lead to fractures and crippling skeletal deformity . Although the U.S. Public Health Service and the World Health Organization officially endorsed the fluoridation of water in the 1950's, some groups continue to oppose the practice. Objectors claim that water fluoridation violates civil rights that fluoride is the *nerve poison*, and that fluoride is unwanted compulsory medication that can have danger side effects. Some groups even claim that fluoridation is a component of conspiracy for national destruction. So far, objectors have been unable to substantiate their claim and the courts have un helped the constitutionality of fluoridation [2].

Researches conducted during the last 5-6 years has also prove that life-long impact and accumulation of fluoride causes not only human skeletal and teeth damages, but also change in DNA structure, paralysis of volition, cancer etc [3]. Because of the toxicity of fluoride and dangers of overdosing, fluoridation of drinking water has been stopped in many countries, for example: German Federal Republic, Sweden, the Netherlands, Czechoslovakia, German Democratic Republic, Soviet Union, Finland, Japan etc [4].

Chloride is one of the major inorganic anion in drinking water. Chloride in surface and ground water originates from both natural and anthropogenic sources, such as the use of inorganic fertilizers, industrial effluents, irrigation drainage, and seawater intrusion in coastal areas [5]. The chloride concentration in water may be considerably increased by treatment processes in which chlorine and chloride is used. Chloride concentration in excess of about 250 milligram per liter can give rise to detectable taste in water, but the threshold depend on the associated cations. Chloride increases the electrical conductivity of water and thus its corrosivity. High chloride content can harm metallic pipes by reacting with metal ions to form soluble salts [6], thus increasing level of metals in drinking water.

Nitrate, highly oxidized form of nitrogen is commonly present in natural water due to end product of the aerobic decomposition of organic nitrogenous matter. Un polluted natural water usually contains only small amount of nitrate. The most common sources responsible for the high level of nitrate are municipal and industrial wastewaters and runoff or leachate from manured or fertilized agricultural lands and urban drainage. The toxicity of nitrate to humans is thought to be solely the consequence of its reduction to nitrate. The most significant health effect associated with nitrate ingestion is methemoglobinemia in infants. This condition results from the presence of high nitrate level in the blood. Methemoglobinemia occurs when hemoglobin, which is the oxygen carrying component of blood, is converted by nitrite to methemoglobinemia, which does not efficiently carry oxygen. Nitrates may act as carcinogens through the formation of N-nitrous compound [7]. Studies in China among populations exposed to high levels of nitrate in drinking water have suggested links between nitrate contamination and stomach and liver cancer [8]. An association between high nitrate level in drinking water and bladder cancer is also reported [9,10].

Phosphorus is the eleventh most abundant element in the earth crust .Where it forms approximately 1120mg/kg.It is geochemically classed as a trace element [11,12]. In the lithosphere it occur as phosphate and these may be leached by weathering processes into hydrosphere. Phosphate may than be precipitated as insoluble metal phosphates that are incorporated into sediments and cycled on geological time scale(millions of year) or it can participate in the rapid terrestrial and aquatic biological phosphorus cycles [13]. Phosphorus exists in water in either a particulate phase or dissolve phase. Particulate matter includes living and dead plankton. The dissolved phase includes inorganic phosphorus and organic phosphorus. phosphorus in water is usually found in the form of phosphate [14]. phosphates can be inorganic form (include orthophosphates and poly phosphates) or organic form(organically bound phosphates). The ortho phosphate is only form determine directly . The other types required pretreatment for conversion to the orthophosphate from for analysis. Phosphates enter the water supply from agricultural fertilizer run-off , water treatment, and biological wastes and residues . Industrial effluents related to corrosion and scale control, chemical processing , and the use of detergents and surfactants contribute significantly . After being dissolved in water , these are converted to orthophosphates at different rates depending upon their types , the temperature of the water , and the pH [15].

Too much of phosphate can cause health problems, such as kidney damage and osteoporosis. Scientific studies have documented that sixty percent (60%) of the radioactivity associated with phosphate is concentrated in clays and sand tailings created by phosphate mining operations. These radiological materials can accumulate in plants, animals and humans. Studies have indicated that phosphate mining may be related to an increased risk of leukemia, lung cancer and colon cancer observed in Florida's mining regions. Many pollutants spread throughout the surficial aquifer are then transported throughout the basin, where they enter the food chains of many species, including humans. Phosphate toxicity can occur with overuse of laxatives or enemas that contain phosphate. Severe phosphate toxicity can result in hypocalcemia, and in various symptoms resulting from low plasma calcium levels. Moderate phosphate toxicity, occurring over a period of months, can result in the deposit of calcium phosphate crystals in various tissues of the body [16].

Sulfate ion is abundantly found in the earth's crust. Low concentration of sulfate may be present in water due to leaching of gypsum, sodium- sulfate and shale. Sulfates also enter into water from sulfur containing organic compounds and industrial water discharge. Sulfate is one of the toxic anions. The presence of sulfate in drinking water can also result in a noticeable taste. Sulfate may also contribute to the corrosion of the water distribution systems. Drinking water may also be contaminated by other anions such as two disinfection by-products: bromide and iodide, there precursors are bromide and iodide. Two suspected carcinogenic substances that occur naturally in drinking water are arsenite and arsinate [17], and mainly perchlorate.

The present research work is based on the analysis of common inorganic anions supply such as fluoride, chloride, nitrate and sulfate in the municipal drinking water.

Fluoride is unique in that the main dietary source is water, not food. The majority of water supplies all over the world are artificially fluoridated. Artificially fluoridated water contains 0.7 to 1.2 milligrams per liter. Fluoride naturally present in drinking water may vary from less then 0.1 milligrams to more than 10.0 milligrams per liter. Bone and teeth contains 99% of the body fluoride. It supports remineralization, and its major function is the prevention of dental carries .

MATERIALS AND METHOD

Experimental Technique

A Metrohm 761 Compact IC with suppressed module, equipped with an anion-separator column (Dual 2) was used for the analysis and the samples were collected from the different locations of Quetta as given in Table-1

Table-1 Locations and Code No.

S.No.	Location	CODE NO.
1	Source water canal	1
2	Source water lake	2
3	Hudda	3
4	Sariab Road	4
5	Debba	5
6	Doctor Bano Road	6
7	Kuchlock	7
8	Mission Road	8
9	Airport	9
10	Askari Park	10
11	Command &Staff College	11
12	Jinnah Road	12
13	Balili	13
14	Liaqat Bazar	14
15	Infantry School	15
16	Mirqalam Koca	16

Reagents and procedures

2.0mmol/L Na_2CO_3 and 1.3mmol/L $NaHCO_3$ were prepared from analytical reagent grade anhydrous sodium carbonate and sodium hydrogen carbonate respectively. The mobile phase and eluent were degassed and filtered using 0.45 µm filters before use. 20mM sulfuric acid was used as a regeneration solution. Calibration standards of appropriate concentration were prepared on a daily basis by diluting IC Multielement standard (Merck) containing 100ppm F^-, 250ppm Cl^-, 500ppm NO_3^- and SO_4^{-2}, and 1000ppm PO_4^{-3}. All solutions were prepared in HPLC grade deionized water. All the working standards and water samples were also filtered before analysis.

Ion chromatography is a popular method for ion analysis because many anions can be determined quickly with higher precision, simultaneously, and different chemical species of the same element can be separated. Anion in test sample is separated by anion chromatographic system containing a guard column, a separator column, and suppressor device and are measured using a conductivity detector [18]. An IC method essentially falls into two categories [19-20]. Suppressed conductometric technique and non-suppressed conductometric technique.

RESU LTS AND DISCUSSION

Distribution of F^-,Cl^-,NO_3, PO_4^{-3}, and SO_4^{-2} contents in source water and tap water samples under study has been shown in Table -2 and by Chromatograms in Fig.1-15 below

.

Table-2 Common Inorganic Anions of groundwater samples

CODE NO.	pH	CODUCTIVITY µs/cm	F- Concentration ppm	Cl- Concentration ppm	NO3- Concentration ppm	PO43¯ Concentration ppm	SO4-2 Concentration ppm
Standard		20.55	2.00	5.00	10	20	20
1	8.05	14.41	14.024	34.35	77.543	186.455	95.01
2		13.95	13.576	48.591	81.557	181.444	94.3
3	8.09	15.804	15.381	42.819	93.763	0	89.05
4		15.216	14.808	40.458	89.749	0	80.54
5	7.49	15.259	14.85	55.299	100.475	0	81.61
6		21.072	20.508	80.516	149.563	0	80.12
7	7.92	14.802	14.405	116.76	199.367	0	79.02
8		20.506	19.957	42.71	113.481	0	106.3
9	7.94	17.527	19.997	21.213	97.696	0	80.32
10		19.406	18.886	44.311	108.246	0	90.07
11	7.6	17.106	16.648	73.391	102.106	0	90.07
12		17.202	16.741	35.362	94.309	0	90.07
13	7.1	16.597	16.153	33.618	90.543	0	95.45
14		17.17	16.71	38.239	95.601	0	78.05
15	7.9	16.706	16.258	61.829	97.385	0	90.07
16		16.368	15.929	44.303	92.423	0	90.07

The fluoride concentration in water sample collected from the different part of Quetta City though very high. This higher concentration of fluoride is most probably due to the industrial effluent discharge of the glass, tiles and ceramics industries, which use fluoride in their processes [21]. The fluoride level of concentration in tap water sample under study is generally higher than the recommended guideline value of WHO, variation of fluoride contents in different part of Quetta City can be denoted as population on the basis of fluoride content.

According to chemical analysis data in the form of concentration (Table-2) the highest content of fluoride (19.1ppm) at Jinnah Road and relatively higher concentration found in Mission Road, and Kuchlak (17.7ppm) which highly populated localities. Water samples of Hudda and Debba also shows high of fluoride, Hudda is not far from the small industries and probably is the influence of the effluents of these industries and Debba is also small industrial area.

Water samples collected from the Mirqalam Koca area representing well developed hilly area shows low concentration (14.6ppm) even less fluoride content than the source water but still higher than the WHO recommended guideline value, which is (1.5ppm) [22].

Significant variation in fluoride concentration in the tap water from different parts of the city reflect most probably to the local factors such as the possible interaction of subsurface water, having variable chemical characteristics, with the tap water due to leakage problem. The variable characteristics of tap water is an anticipated mostly due to variable density of the population with poor to good drainage conditions and the type of industry operating in the localities . The higher concentration of fluoride in tap water needs immediate attention of the local authorities for monitoring normal concentration of fluoride in water from health point of view. The chloride concentration in the water samples collected from the different part of the Quetta City though very low than the WHO recommended guideline values which is may be due to improper treatment processes or inefficient quantity of chlorine or chloride is used. Water sample of Balili is highly chlorinated, concentration of chloride about (81.4ppm), which may be due the mixing of municipal water with ground water or improper treatment of drinking water. Water sample collected from Mirqalam Koca shows very low concentration than the WHO

Fig 1: Chromatogram of standard F^-,Cl^-, NO_3^-, PO_4^{-3} and SO_4^{-2}

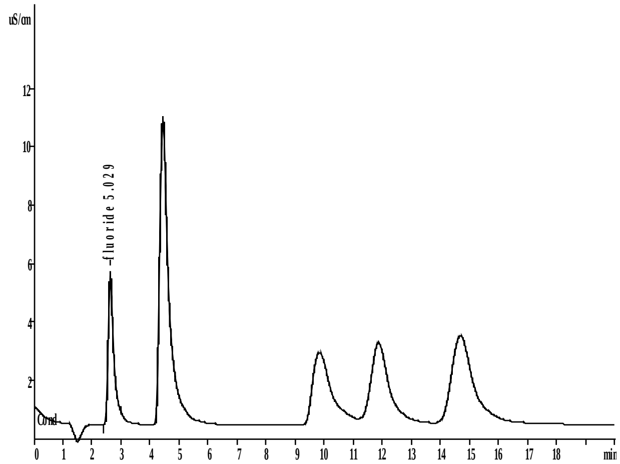


Fig 2: Chromatogram of Airport ground water sample

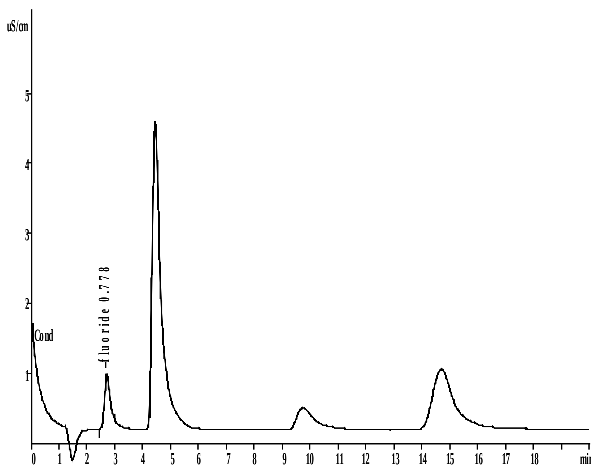


Fig 3: Chromatogram of Balili ground water sample

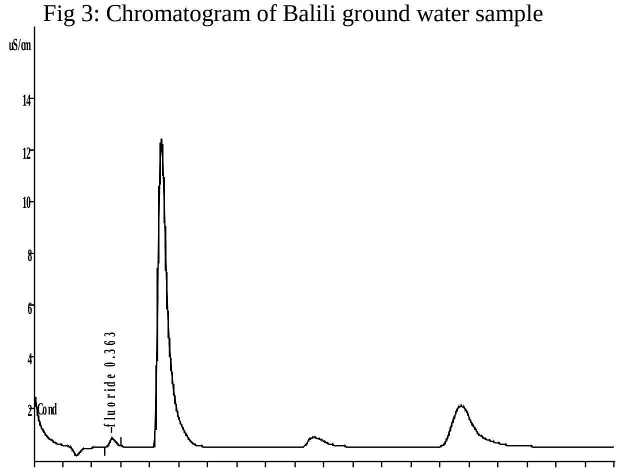


Fig 4: Chromatogram of Askari Park ground water sample

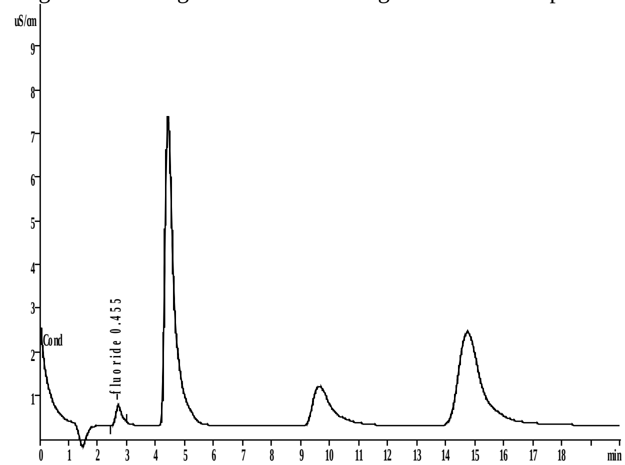


Fig 5: Chromatogram of Jinnah Road ground water sample

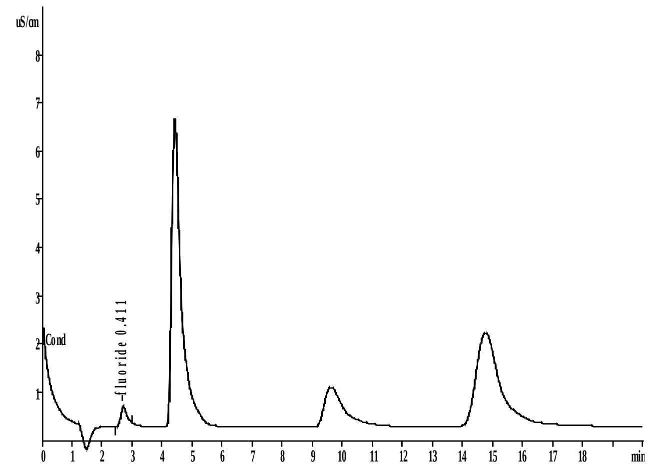


Fig 6: Chromatogram of Sariab Road ground water sample

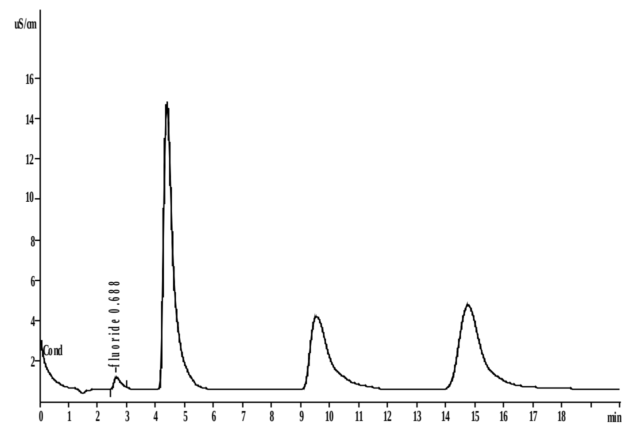


Fig 7: Chromatogram of Infantry School ground water sample

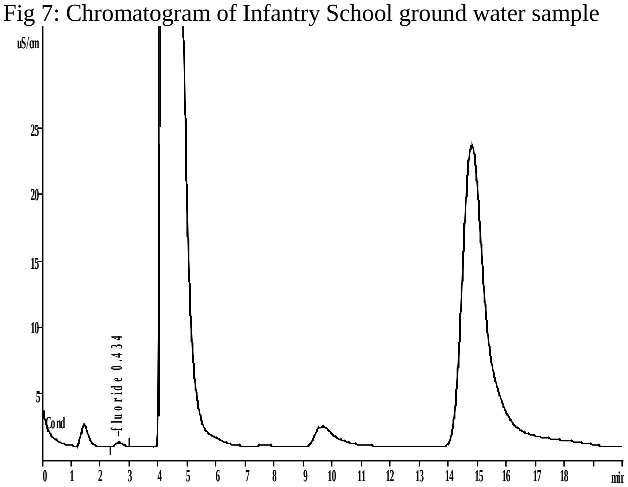


Fig 8: Chromatogram of Mission Road ground water sample

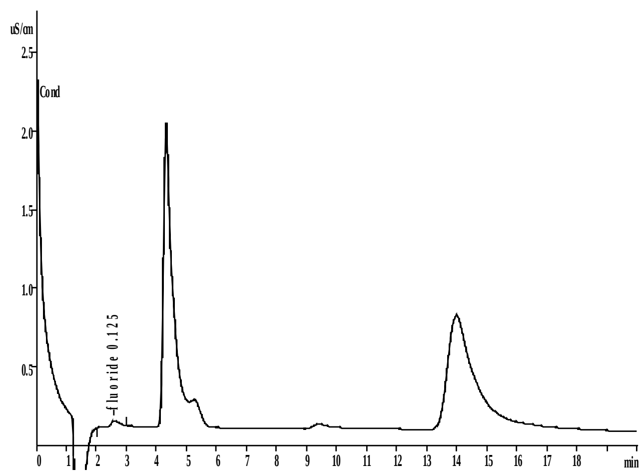


Fig 9: Chromatogram of Liaqat Bazar ground water sample

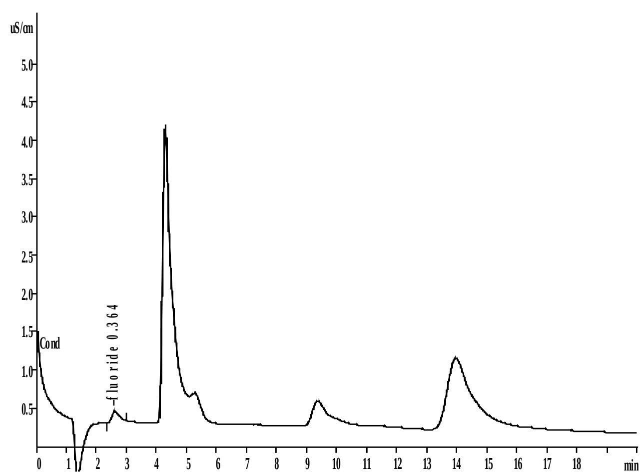


Fig 10: Chromatogram of Kuchlock ground water sample

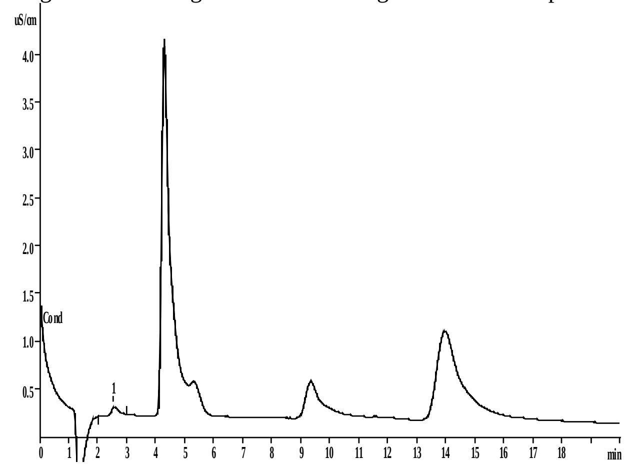


Fig 11: Chromatogram of Hudda ground water sample

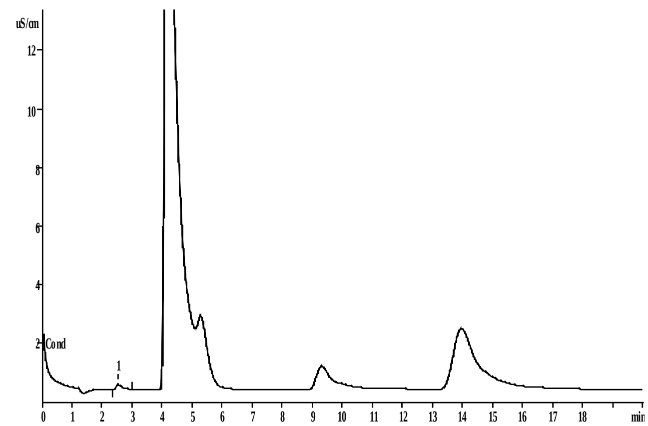


Fig 12: Chromatogram of Debba ground water sample

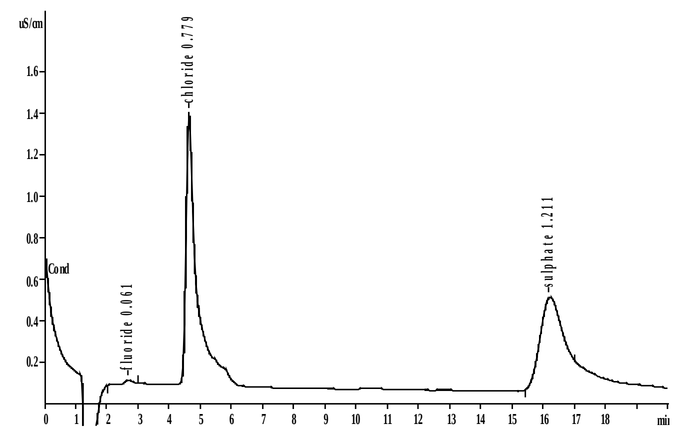


Fig 13: Chromatogram of Doctor Bano Road ground water sample

Fig 13: Chromatogram of Doctor Bano Road ground water sample

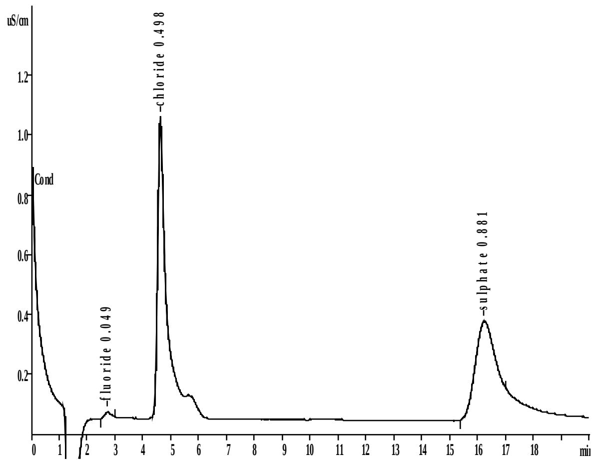
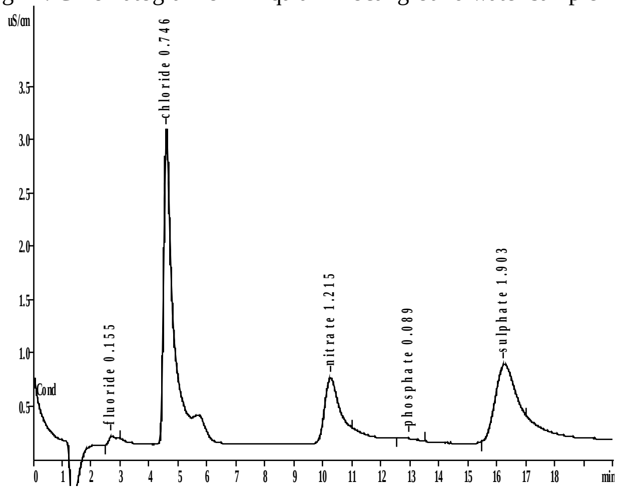
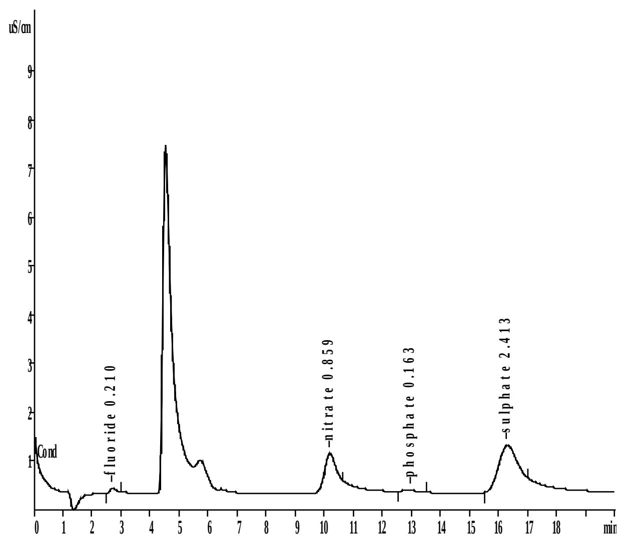


Fig 14: Chromatogram of Mirqalam Koca ground water sample



. Fig 15: Chromatogram of Command & Staff College ground water sample



recommended guideline values.

According to the data obtain from different areas of Quetta city shows highest content of nitrate. Water sample of Jinnah Road maximum contaminated with NO_3^-, which is (99.3ppm). The nitrate concentration in tap water samples is normally low according to WHO recommended guideline values which is (50.0ppm) [22], but excessive nitrate concentration may indicate the presence of heavy fertilizer runoff or excessive discharge from a waste treatment facility .High nitrate levels in water can cause methemoglobinemia or blue baby syndrome, a disease that effect the oxygen carrying capacity of infant's blood usually resulting from the consumption of high levels of nitrate. Prolonged intake of high levels of nitrate linked to the gastric problems due to the formation of nitrosamines, which can cause cancer. So, protection of drinking water supply from contamination is important for health.

Drinking water is also contaminated with sulfate, but WHO can not recommended any guideline for sulfate content in water. Results shows high concentration of sulfate in Mission Road (106.3ppm) , and very low concentration found in Mirqalm Koca water sample (2.1 ppm). Higher concentration of sulfates may be due to the discharged into water from mines, smelters, paper machines and textile works . Levels of sulfates in rain and surface water correlate with emission levels of sulfur dioxide from anthropogenic sources.

CONCLUSION

Overall, higher concentration of anions in tap water samples and source water indicate to the local factors such as leakage and seepage interaction between water supplies and sewage line. Other possible cause may be attributed to the mixing of tube well water into river water before supply. Another possible factor, which is to be considered into connection, is the dilution factor of ground water by the river water which can show variable results so far as the bulk chemical constituents changes are concerned. Inorganic anions concentration in source water and tap water under the study is generally higher than the recommended guideline of WHO, Therefore source water and tap water should be thoroughly monitored for its anion contents before supply for health point of view.

REFERENCES

1. John Fawell and Mark J Nieuwenhui jsen, Contaminants in drinking water: Environmental pollution and health, *British Medical Bulletin*,2003, 68, 199-208.
2. Paul Insel; R. Elaine Turner, R. D and Don Ross, *Nutrition*, 2nd ed. Jones and Bartlett publishers Toronto, 448, 449, 494, 495, 2004:.
3. Yelana Veressinina, Marina Trapido, Viktor Ahelik, and Rein Munter, Fluoride in drinking water: The problem and its possible solution,*Proc. Estonian Acad. Sci.Chem*., **50**(2), 81-88, 2001.
4. R. Ziegelbecker, Fluoridation in Europe, *Fluoride*,, **31**, 171-174, 1998.
5. Department of national Health and welfare(Canada), Guideline for Canadian drinking water quality. *Supporting documentation*, Ottawa, 1978.
6. Sodium, chlorides, and conductivity in drinking water: a report on a WHO working group, Copenhagen , WHO regional office for Europe, 1978.

7. S. S. Mirvish, Q Huang, S.C. Chen, D. F. Birt, G.W.Clark, R.A.Hinder, T.C. Amyrk, T.R. De Meester, Metabolism of carcinogenic nitrosamines in the rat and human esophagus and induction of esophageal adenocarcinma in rats, *Endoscopy*, **25**: 627-631, 1993.
8. X. G. Tao, H.G. Zhu, S.Z.Yu, Z.Y.Zhao, J.R.Wang, G.D.Wu, X.F.You, C.Li, W.L.Zhi, J.P.Bao, Z.Ce.Sun, Effect of drinking water from the lower reaches of the Hung Pu River on the risk of male stomach and liver cancer death, *Public Health Rev.*, **19**, Page, 229-236, 1992.
9. M. H. Ward, K. P. Cantor, D. Riley, S. Merkle, C.F.Lynch, Nitrate in public water supplies and risk of bladder cancer, Epidemiology, **14**, 183-190, 2003.
10. John Fawell and Mark J Mieuwenhui jen, contaminants in drinking water: Environmental pollution and health, *British Medical Bulletin.*, **68**, 199-208, 2003.
11. VE MeKelvey. Abundance and distribution of phosphorus in the Lithosphere, In: E. J. Griffith, A Beeton, J. M. Spencer, D. T. Mitchell, *Environmental phosphorus Handbook.* New York, Wiley-Interscience, 718, 1973.
12. NN Greenwood, A. Earnshaw, Chemistry of the Elements, Oxford, Pergamon Press, 1984.
13. I. D. McKelvie, D Peat, P. J. Worsfold, Techniques for the separation of and quantification of phosphorus in natural waters, *Anal Proc*., 32, 437-445, 1995.
14. Leo. M. L. Nollet, Hand book of water analysis, food science and technology (Marcel Dekker, Inc), New York, 1948, 67, 273-294.
15. Water Hand *Book of Analysis Procedure*: Phosphate Ortho, APHA Standard methods, 12, 231, 1965,
16. Nadra, *et al.* Proinflammatory Activation of Macrophages by Basic Calcium Phosphate Crystals via Protein Kinase C and MAP Kinase Pathways: I viscious Cycle of Inflammation and Arterial Calcification? *Circ Res*; **96**; 1248-1256, 2005.
17. Arnaud Dudoit and Spiros A. Pergantis, Ion chromatography in series with conductivity detection and inductively coupled plasma mass spectrophotometry for the detection of mine halofel, metalloid and non metal species in drinking water**,** *J.Anal.At.Spectrom*., **16**, 575-580, 2001.
18. Leo. M. L. Nollet, *Hand book of water analysis*, food science and technology (Marcel Dekker, Inc), New York, **67**, 273-294, 1948.
19. M. A. Tabatabai, Marcel Dekker, Inc, New York, **67**, 391-393, (1948).
20. S. V. Kamarkar, ion chromatography, *Environmental analysis and remediation*. Wiley, New York, 2391-2404, 1998.
21. Gunnlaugsson, Thorfinnur; Kruger, Paul E.; Jensen, Paul; Tierney, Julian; Ali, Haslin Dato Paduka; Hussey, Gillian M. Colorimetric "Naked Eye" Sensing of anions in aqueous solution, *Journal of Organic Chemistry*, 70(26), 10875-10878, 2005.
22. Ramkumar, Jayshree, Synthesis and characterization of lanthanum chloranilate complex: Application to spectrophotometric determination of anions, *Talanta* **68**(3), 902-907, 2006.