

Validation and Quantification of Some Trace Elements in Drinking Water and Wells from Turabah Province, KSA by ICP-OES

Malik Abdalla Abdelrahman Elsheikh^{1,2}, Dafaalla Mohamed Hag Ali^{1,2}, Awad Abdalla Momen^{1,3} and Mohammed Awad Ali Khalid^{1,4}

¹Department of Chemistry, Faculty of Applied Medical Sciences (Turabah Branch), Taif University, Taif, Saudi Arabia.

²Department of Chemistry, College of Sciences Sudan University of Science and Technology, Khartoum, Sudan.

³Department of Chemistry, College of Applied and Industrial Sciences, Bahri University, Khartoum, Sudan.

⁴Department of Chemistry, Faculty of Science, University of Khartoum, Khartoum, Sudan.

Accepted 07 Jan 2015, Available online 01 Feb 2015, Vol.3 (Jan/Feb 2015 issue)

Abstract

Concentration of 12 trace elements (TEs) Na, K, Ca, Mg, Fe, Zn, B, Al, Pb, Cd, As and Sr, was determined in drinking water of local and national factories and wells in Turabah Province (KSA) by using Inductively coupled plasma-optical emission spectrometry (ICP-OES) technique after pre-concentration and acid digestion. The results show that the concentrations of Na, K, Ca, Mg, Fe, Zn, Al, Pb, Cd and As in the samples of the local factories in Turabah Province and national factories (KSA) are below the maximum level that recommended by World Health Organization (WHO) and Saudi Arabia Standards Organization (SASO). While, the concentrations of B are above the maximum level recommended by SASO. The results of the wells samples show that the concentrations of Fe, Zn, Al, Pb, Cd and As are below the maximum level that recommended by WHO and SASO while the concentrations of Na, K, Ca, Mg and B are above and below the maximum level recommended by SASO according to the source of sample. The recovery percent was found to be 97.5 - 99.5%. The method was validated in terms of accuracy, precision, limit of detection (LOQ) and limit of quantification (LOD) and confirmation reliability.

Keywords: Trace Elements, Drinking Water, Ground Water, ICP-OES

1. Introduction

Turabah Province (Taif area, KSA) is depends on ground water as a main source of drinking for both humans and animals, food preparation and agriculture activities. Groundwater contains major ions, trace metals and other toxic pollutants (Zubairet *et al.*, 2008). The concentration of these substances in the aquifers is a function of the geological environment, composition of water, effect of storm water infiltration, water movement, its velocity, land use, rainfall and recharge mechanism. Some trace elements (TEs) may be essential to normal body functions and enzyme activities such as calcium (Ca), magnesium (Mg), sodium (Na), copper (Cu), and zinc (Zn). Drinking water may contain high levels of these elements, or other toxic elements such as aluminum (Al), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) and selenium (Se), that may be hazardous to human health. The worst part of TEs is that once they build up in the body. They can cause irreversible damages to the body organs. The toxicity of TEs depends mainly on its chemical form, route of exposure, bioavailability, distribution, storage in the body and excretion parameters (Hussainet *et al.*, 2012). The abnormal metabolism of these elements plays an

important role in health and disease conditions, and studies about them have been attracting significant interest. It has been speculated that TEs may play a role in the pathogenesis of many diseases. Some of them form part of enzymes and others are involved in the synthesis of hormones (Nadicaet *et al.*, 2003, Afridiet *et al.*, 2011). Others are known to be associated with certain diseases if they are present in the body in abnormally low concentrations. Several of them have been documented as being involved in blood pressure control and others may lead to intoxications in humans, if ingested in high concentrations. Many of them are excreted primarily in urine and some are transmitted to blood (Forreret *et al.*, 2001, Momenet *et al.*, 2013). TEs have been attracting the attention of scientists in various systems related to human health such as clinical and environmental analysis (Momen & Lilly, 2010). World Health Organization (WHO) places great emphasis on the quality of drinking water and has recommended upper limits for a number of TEs for drinking water (WHO, 1977 & 1980).

Sodium at normal intake levels is beneficial to healthy adults. However, people with heart disease or hypertension should reduce sodium intake to lower the blood pressure (WHO, 1996). Epidemiological and clinical

studies show that a high-potassium (K) diet lowers blood pressure in individuals with both raised blood pressure and average population blood pressure. Prospective cohort studies and outcome trials show that increasing K intake reduces cardiovascular disease mortality. This is mainly attributable to the blood pressure-lowering effect and may also be partially because of the direct effects of K on the cardiovascular system. An increased K intake lowers urinary Ca excretion and plays an important role in the management of hypercalciuria and kidney stones and is likely to decrease the risk of osteoporosis (He FJ, 2008). Drinking water containing Ca that may provide a significant portion of the required daily intake to prevent such ailments as osteoporosis, hypertension, and cardiovascular disorders (WHO, 1996). Magnesium is quickly expelled from the bodies of healthy humans.

People with kidney disease, however, may suffer from hypertension, confusion, muscle weakness, and coma (WHO, 1996, 2009). Iron is an essential element in human nutrition. The estimates of the minimum daily requirement for Fe depend on age, sex, physiological status, and Fe bioavailability and range from about 10 to 50 mg/day. Iron in water is not a health hazard by itself but it may increase the hazard of pathogenic organisms, since many of these organisms require Fe to grow (WHO, 1996). Most biochemical roles of Zn reflect its involvement in a large number of enzymes or as a stabilizer of the molecular structure of subcellular constituents and membranes (WHO, 1996). Zinc participates in the synthesis and degradation of carbohydrates, lipids, proteins and nucleic acids. Zinc leads to poison and irritate the digestive system (upset stomach), causing a lack of absorption of Cu and body temperature will be raised which will affect body immunity (Khun& Liu 2009). Aluminum is the most abundant metal in the earth's crust and therefore is likely to be present at some level in most ground water. The correlation of Al consumption to nervous system disorders is being researched (WHO, 1997). The positive relationship between Al in drinking-water and Alzheimer disease (AD) was demonstrated in several epidemiological studies (WHO, 1996, 1997).

Arsenic in drinking water is one of the most serious environmental health hazards faced by populations in many areas of the world. Arsenic is highly toxic and can lead to a wide range of health problems (Smedley & Kinniburgh, 2002, Plant J. A., 2003). Also As is carcinogenic, mutagenic and teratogenic (National Research Council, 1999). Symptoms of chronic arsenic poisoning are weight and hair loss, nausea, white lines across the toenails and fingernails, depression, and general fatigue. Cadmium usually accumulates in the liver and kidney, particularly in the kidney cortex. Manifestations of Cd toxicity such as histological changes in the kidney, liver, testes, pancreas, bowels and blood vessels (Maroof *et al*, 1986 & 1990, Ling *et al*, 1988, Nogawa *et al*, 1979). Lead is classified as a category 2B

carcinogen by the International Agency for Research on Cancer (IARC, 1987). Lead is a cumulative poison, meaning that it remains in the body following exposure. Children under age three are most susceptible to lead poisoning. Minor symptoms include abdominal pains, decreased appetite, constipation, fatigue and decreased physical fitness. Long-term exposure may cause kidney damage, anemia, nerve and brain damage, and death (WHO, 1996). Boron can affect the function or composition of several body systems, including the brain, skeleton and immune system, generally in a beneficial fashion. Moreover, homeostatic mechanisms apparently exist for B because it is rapidly excreted in the urine, does not accumulate in tissues, and is maintained in a relatively narrow range of concentrations in blood of healthy individuals (Forrest, 1997). Toxic symptoms due to overdosing of Sr have not been reported in man. However, intravenous administration of high doses of Sr induces hypocalcaemia due to increased renal excretion of calcium. It was reported many years ago that high dietary Sr produced insoluble strontium phosphates leading to phosphorus deficiency and to rickets, *vide infra*. The only stable strontium-containing chemical that is considered to be harmful to humans in small amounts is strontium chromate, the toxicity being caused by the Cr which is a genotoxic carcinogen (Nielsen, 2004).

Determination of TEs is still an active topic in analytical science. There are various techniques for the analysis of TEs in water samples. The choice of an analytical technique depends on a number of factors, including susceptibility to matrix effects, the range of elements covered, the detection limits and suitability for the matrix of interest. The susceptibility of an analytical technique to matrix effects depends on the sample composition. With some matrices, these effects are of major importance, but others can be avoided by a modification of the technique. The usefulness of an analytical method for TEs analysis also depends on the range of elements covered and the order of magnitude of its detection limits (DL) for the elements at the top and bottom of its sensitivity range. Detection limits will not be the same for all elements, so that simultaneous multielements determination will require compromises in experimental conditions that will affect the accuracy and precision of at least a few elements (WHO, 1996).

Inductively Coupled Plasma–Optical Emission Spectrometry (ICP–OES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, and can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation (Fassel, 1976, Merryfield and Loyd, 1979). Also, ICP–OES is a well establish analytical technique with large linear dynamic range, low detection limits, high precision and accuracy, which offers automation, rapid multi-element analysis for the determination of major, minor and TEs in water samples.

Some TEs present in very low concentration, this is depend on the type of the sample and it is source. In this case pre-concentration is necessary to reach the low DL. Although potentially usefulness and harmful effects of trace elements are generally well known, limited studies are available regarding the hazardous of these elements. Therefore, the present study aimed to determine the concentration of TEs including Na, K, Ca, Mg, Fe, Zn, B, Al, Pb, Cd, As and Sr in drinking and wells water samples of local (LF) and national (NF) factories from Turabah Province (KSA) by using ICP-OES. A total of 18 (well samples), 18 (local factories samples) and 6 (national factories samples) were analyzed after samples pre-concentration using ICP-OES. Another aim of this study is to compare the obtained values of determined TEs with those values that recommended by World Health Organization (WHO) and Saudi Arabia Standards Organization (SASO).

2. Materials and methods

2.1 Reagent and glassware's

All reagents and chemicals were of analytical grade obtained from Merck (Darmstadt, Germany, www.merck.de). Nitric acid of analytical grade R. Was used, 69–72 % (m/m) HNO_3 ($d = 1.41\text{--}1.51 \text{ kg l}^{-1}$), De-ionized doubly distilled water (DDDW) was also used throughout the analyses for preparing reagents, standard and sample solutions. DDDW also was used for washing and rinsing of all apparatus and glassware. Acid-washed polyethylene bottles were used for preparing and storing solutions. All solutions were stored in the refrigerator until needed for analysis. Polyethylene storage bottles, glassware and the auto sampler cups were cleaned by soaking in 5 mole $\text{l}^{-1}\text{HNO}_3$ for about 24 hrs, rinsing five times with DDDW, dried, and stored in a class-100 laminar-flow hood.

2.2 Samples Collection and Preparation

2.2.1- Well samples

Eighteen different representative samples (1000 cm^3 of each) were collected from different six wells. These wells were far away from each other ($\sim 10\text{--}80$ kilometer) in the valley of Turabah Province. They kept in polyethylene storage bottles (metal free containers have been used) after soaking the bottles in dilute nitric acid (5 mole $\text{l}^{-1}\text{HNO}_3$) overnight and washed with double DDDW and then rinsed three times with the water sample before taken. The samples were been taken at different interval of period, The season of sample collections, the depth and the age of each well in the valley of Turabah Province was also recorded. Samples were filtrated through a $0.45 \mu\text{m}$ pore diameter membrane filter at the time of collection. The pH of each sample at the time of collection was also measured, then maintained in the refrigerator.

One hundred cm^3 of each sample was transferred into 250 cm^3 conical flask, 5 cm^3 of 5.0 % HNO_3 was added to it and then evaporated to about 10 cm^3 by using adjustable hot plate (95°C). Sample was cooled and transferred to 50 cm^3 volumetric flask. The residue was washed with 5 cm^3 of 5.0% HNO_3 and with DDDW, and the volume was completed with DDDW to the mark. All prepared samples were maintained in the refrigerator until needed for analysis.

2.2.2 Local and national factories samples

Eighteen Different representative samples (1000 cm^3 of each) were collected from three local factories in Turabah province. Also, six different representative bottled samples (1000 cm^3 of each) that represent two different national factories in KSA were also collected from different markets in Turabah Province. The samples kept in polyethylene storage bottles (metal free containers have been used) after soaking the bottles in dilute nitric acid (5 mole $\text{l}^{-1}\text{HNO}_3$) overnight and washed it with DDDW and then washed three times with the collected water sample before taken. Samples were taken at different interval of period. For internal purposes and comparison reasons water treatment method of each factory was recorded and the type of bottle and the production date of national factories samples were recorded. The samples were filtrated through a $0.45 \mu\text{m}$ pore diameter membrane filter at the time of collection and the pH of each sample was measured then maintained in the refrigerator. Five hundred cm^3 of each sample was transferred into 1000 cm^3 conical flask, 5 cm^3 of 5.0 % HNO_3 was added to it and then evaporated to about 10 cm^3 by using adjustable hot plate (95°C). Then, the sample was cooled and transferred to 50 cm^3 volumetric flask. The residue was washed with 5 cm^3 of 5.0% HNO_3 and with DDDW, and the volume was completed with DDDW to the mark. All prepared samples were maintained in the refrigerator until needed for analysis.

2.3 Instrumentation and conditions

A Varian 725-ES inductively coupled plasma-optical emission spectrometer (ICP-OES), with radial viewing configuration (Perkin Elmer, USA), was used to analyze the standard and the sample solutions of Na, K, Ca, Mg, Fe, Zn, B, Al, Pb, Cd, As and Sr. The ICP-OES operating conditions were well optimized and carefully selected in order to maximize the sensitivity for the desired elements and to obtain the best precision and accuracy. Details of the operating conditions are summarized in Table 1. The LOD and the LOQ from 1% HNO_3 for the determined element are shown in Table 2.

2.4 Statistical analysis

All results were statistically evaluated by Student *t*-test and ANOVA test ($p=0.05$). In addition, Microsoft Excel and

Origin software's were also used to assess the significance of the differences between the variables investigated in well, local and national factories samples. The concentration values obtained were expressed as mean value \pm standard deviation ($p=0.05$). All statistical analyses were based upon triplicate measurements of all standards and sample solutions.

3. Results and discussion

The method was validated in terms of accuracy, precision, limit of detection (LOD) and limit of quantification (LOQ) and confirmation reliability (Elgorashe et al, 2014, M. Thompson et al, 2002). All results were expressed as $x \pm s$, where x mean values and s is standard deviation. To ensure that no contamination and/or loss of elements occurs during sample preparations and measurement methodology, a multi-element standard solution was prepared in DDDW and treated in a similar way to samples solutions. The recoveries percentage (%) was found to be 97.3- 99.6%. The LOD and the LOQ from 1% HNO₃ for the determined elements were shown in Table 2. The relative standard deviations (RSDs) for the samples were show in Tables 3A and 3B. The method was validated from the results of recoveries%, LOD, LOQ and RSDs and it was found to be reliable, accurate and precise. The calculation of the recovery percent were carried out by using the following equation (U.S. Environmental Protection Agency, 1994).

$$R = (LFB - LRB) \times 100 / s$$

Where:

R = recovery percent

LFB = laboratory fortified blank

LRB = laboratory reagent blank

s= concentration equivalent of analyte added to fortify

The pH of the all samples (Table 4) are within the recommended range (pH = 6.5-8.5). The pH of most samples is slightly alkaline.

Table 5 and Figure. 1 show the concentrations values of the elements Na, K, Ca , Mg and Fe of the local factories (LF)samples and the national factories (NF) samples, the results show that all the concentrations are below the maximum level that recommended by WHO and SASO (Table 6) except B which is above the maximum level that recommended by SASO in some samples but all samples are below the maximum level that recommended by WHO. That is mean the water is safe for drinking. The results of Na, K and Ca are also below the value obtained by Zahid, W. M. In KSA while Fe values are in the same range (Zahid,2003). Figure 2 and 3 shows that the real concentration value of the national factories samples compared to the concentration values written on the label(Table 7),it was found that they are almost around the labels values. Table 5 and Figure 4 show the concentrations values of TEs Zn, B, Al, Pb, Cd, As and Sr.

The results show that all the concentrations are below the maximum level that recommended by WHO and SASO (Table 6). According to the limit of detection the results show the absent of the TEs Pb, Cd and As, while B recorded the higher concentrations values among these elements.

Table 8 and Figure 5 show the concentrations values of the TEs Na, K, Ca and Mg, of the wells samples. Well 6 show very high concentration of the TEs Na, Ca, and Mg (1586.94 \pm 75.04, 1281.293 \pm 61.95 and 692.615 \pm 10.75ppm respectively), well 4 samples also show high concentration values of the TEs Na, Ca, and Mg (473.195 \pm 20.42, 392.129 \pm 26.72 and 149.579 \pm 5.08 respectively),while well 1, 2, 3 and 5 showed low concentrations values of the mentioned elements.

Table 8 and Figure 6 show the concentrations values of the TEs Fe, Zn, B, Al, Pb, Cd, As and Sr of the wells samples. The results show that the concentrations of the TEs Fe, Zn, B and Al are below the maximum level that recommended by WHO and SASO (Table 6). Pb and As are detected only in well 6below the maximum level that recommended by WHO and SASO, while Cd detected only in well 4 and well 6 samples, bellow the maximum level that recommended by WHO and SASO, indicating the safety of water from view of these elements.

Sr is detected in all samples under study, wells and factories samples, but no health-based guideline values are proposed for Sr. Toxic symptoms due to overdosing of Sr have not been reported in man. However, intravenous administration of high doses of Sr induces hypocalcaemia due to increased renal excretion of Ca. The only stable Sr containing chemical that is considered to be harmful to humans in small amounts is strontium chromate, the toxicity being caused by the chromium (not Sr) as mentioned in the literature. Figure 5 shows the comparisons of Na, Ca, K and Mg values at different wells samples, it was found that Well 6 shows high concentration of. Na, Ca, and Mg compared to other well samples. While Figure 6 shows the comparisons of Fe, Zn, B, Al, Pb, Cd, As and Srvalues at well samples. Well 6 shows elevated Sr compared to other well samples.

Correlation between concentrations of Mg and Sr, Mg and Ca, Ca and Sr were studied and the relation coefficients were calculated (Table 9), it was found that there are strong correlation between concentration of these elements in the wells samples ($r > 0.99$), while this correlation is absent in the factories samples ($r < 0$). Strontium is associated with calcium in nature, and is found chiefly as the form of the sulfate mineral celestite (SrSO_4) and the carbonate strontianite (SrCO_3). It is associated with limestone and calcite (Stringfield,1966). In groundwater strontium behaves chemically much like presence of calcium ions, strontium commonly forms co-precipitates with calcium minerals such as calcite and anhydrite at an increased pH. This point explained why Sr associated with Ca and have high value of r ($r = 0.9961$) alkaline.

Table 1: ICP–OES operating parameters for determination of selected TEs

| Parameters | Conditions |
|--------------------------|------------|
| Power (kW) | 1.20 |
| Plasma flow rate (L/min) | 15.0 |
| Auxiliary Flow (L/min) | 1.50 |
| Viewing height (mm) | 10 |
| Nebulizer Pressure (kPa) | 250 |
| Replicate read time (s) | 7 |
| Sample uptake delay (s) | 30 |
| Pump rate (rpm) | 20 |
| Rinse time (s) | 25 |
| Replicates | 3 |

Table 2: LOD and LOQ for determination of selected TEs

| Element | Wavelength (nm) | LOD | LOQ |
|---------|-----------------|---------|---------|
| Na | 589.592 | 0.0360 | 0.0795 |
| K | 766.491 | 0.0318 | 0.07876 |
| Ca | 317.933 | 0.12813 | 0.26611 |
| Mg | 279.8 | 0.0164 | 0.0447 |
| Fe | 238.204 | 0.0062 | 0.01318 |
| Zn | 213.857 | 0.0022 | 4.5598 |
| B | 249.678 | 0.0024 | 5.64196 |
| Al | 396.152 | 0.0055 | 12.8645 |
| Pb | 220.353 | 0.0148 | 37.5263 |
| Cd | 214.439 | 0.0009 | 2.38979 |
| As | 188.98 | 0.0281 | 64.5057 |
| Sr | 421.552 | 0.0005 | 1.2391 |

Table 3 (A): The relative standard deviation (RSD) for the factories samples

| Element | RSD | | | | | |
|---------|-------------------------|------|------|----------------------------|------|--|
| | Local factories samples | | | National factories samples | | |
| | 1 | 2 | 3 | 1 | 2 | |
| Na | 2.17 | 3.36 | 0.27 | 3.13 | 0.43 | |
| K | 0.17 | 3.70 | 0.45 | 9.90 | 1.43 | |
| Ca | 1.01 | 2.02 | 0.07 | NC | 0.36 | |
| Mg | 1.72 | 4.44 | 4.03 | 0.52 | 3.85 | |
| Fe | 10 | 10 | 6.67 | 0 | 8.33 | |
| Zn | 0 | 10 | 0 | NC | NC | |
| B | 1.32 | 8.96 | 7.44 | 4.09 | 7.60 | |
| Al | 3.68 | 5.88 | 4.26 | 0 | 1.15 | |
| Pb | NC | NC | NC | NC | 10 | |
| Cd | NC | NC | NC | NC | NC | |
| As | NC | NC | NC | NC | NC | |
| Sr | 0 | 2.22 | 1.47 | 0 | 2.86 | |

NC= not calculated

Table 3 (B): The relative standard deviation (RSD) for the wells samples

| Element | RSD | | | | | |
|---------|---------------|-------|------|-------|-------|-------|
| | Wells samples | | | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | |
| Na | 0.88 | 2.09 | 2.66 | 4.32 | 3.78 | 4.73 |
| K | 1.13 | 0.91 | 2.84 | 4.17 | 2.86 | 2.71 |
| Ca | 0.83 | 2.59 | 0.26 | 7.18 | 8.19 | 4.84 |
| Mg | 8.32 | 6.54 | 1.28 | 3.40 | 4.05 | 1.55 |
| Fe | 1.43 | 2.63 | 4.17 | 3.33 | 0 | 11.11 |
| Zn | 10 | 9.68 | 0 | NC | NC | NC |
| B | 9.01 | 10.53 | 3.57 | 2 | 4.02 | 3.25 |
| Al | 8.13 | 0.68 | 4.35 | 11.04 | 11.00 | 5.59 |
| Pb | NC | NC | NC | NC | NC | 6.67 |
| Cd | NC | NC | NC | 0 | NC | 0 |
| As | NC | NC | NC | NC | NC | 0 |
| Sr | 1.02 | 1.79 | 1.71 | 3.80 | 3.71 | 5.37 |

NC= not calculated

Table 4: The pH of the factories and the wells samples

| Sample | LF.1 | LF.2 | LF.3 | NF.1 | NF.2 | W.1 | W.2 | W.3 | W.4 | W.5 | W.6 |
|--------|------|------|------|------|------|-----|-----|-----|-----|-----|-----|
| pH | 8.0 | 8.0 | 8.1 | 7.5 | 7.6 | 8.5 | 8.6 | 8.1 | 7.8 | 8.2 | 7.6 |

Table 5: Concentration (ppm) of the elements in different factories samples

| Element | Concentration (ppm) | | | | |
|---------|-------------------------|-------------|-------------|----------------------------|--------------|
| | Local factories samples | | | National factories samples | |
| | 1 | 2 | 3 | 1 | 2 |
| Na | 18.400±0.4 ^a | 8.490±0.20 | 11.260±0.03 | 1.920±0.06 | 11.509±0.05 |
| K | 0.580±0.001 | 0.540±0.020 | 0.660±0.003 | 0.101±0.01 | 0.070±0.001 |
| Ca | 3.980±0.04 | 4.950±0.10 | 6.950±0.005 | ND | 14.054±0.05 |
| Mg | 1.160±0.02 | 1.35±0.06 | 1.986±0.08 | 19.410±0.1 | 2.077±0.08 |
| Fe | 0.030±0.003 | 0.03±0.003 | 0.015±0.001 | 0.007±0.000 | 0.012±0.001 |
| Zn | 0.003±0.000 | 0.010±0.001 | 0.010±0.000 | ND | ND |
| B | 0.760±0.01 | 0.670±0.06 | 0.806±0.06 | 0.734±0.03 | 1.316±0.1 |
| Al | 0.190±0.007 | 0.170±0.01 | 0.188±0.008 | 0.054±0.000 | 0.174±0.002 |
| Pb | ND | ND | ND | ND | 0.005±0.0005 |
| Cd | ND | ND | ND | ND | ND |
| As | ND | ND | ND | ND | ND |
| Sr | 0.031±0.000 | 0.045±0.001 | 0.068±0.001 | 0.004±0.0000 | 0.007±0.0002 |

a: a mean value ± standard deviation (n=3), ND= not detected

Table 6: WHO and SASO Guide line for TEs

| Element | Concentration (ppm) | |
|---------|---------------------|---------------|
| | WHO standard | SASO standard |
| Na | 200 | 100 |
| K | NA | NA |
| Ca | NA | 75 |
| Mg | NA | 30 |
| Fe | 0.2 | 0.3 |
| Zn | 3 | 3 |
| B | 2.4 | 0.5 |
| Al | 0.2 | 0.2 |
| Pb | 0.01 | 0.01 |
| Cd | 0.003 | 0.003 |
| As | 0.01 | 0.01 |
| Sr | NA | NA |

NA= not available

Table 7: Concentration (ppm) of the elements according to factories labels

| Element | Concentration (ppm) | |
|---------|------------------------|-----------------------|
| | National factories (1) | National factories(2) |
| Na | 13 | <6 |
| K | 0.2 | <0.5 |
| Ca | 12 | <3 |
| Mg | 1.5 | <15 |
| Fe | 0.0 | <0.01 |

<= less than

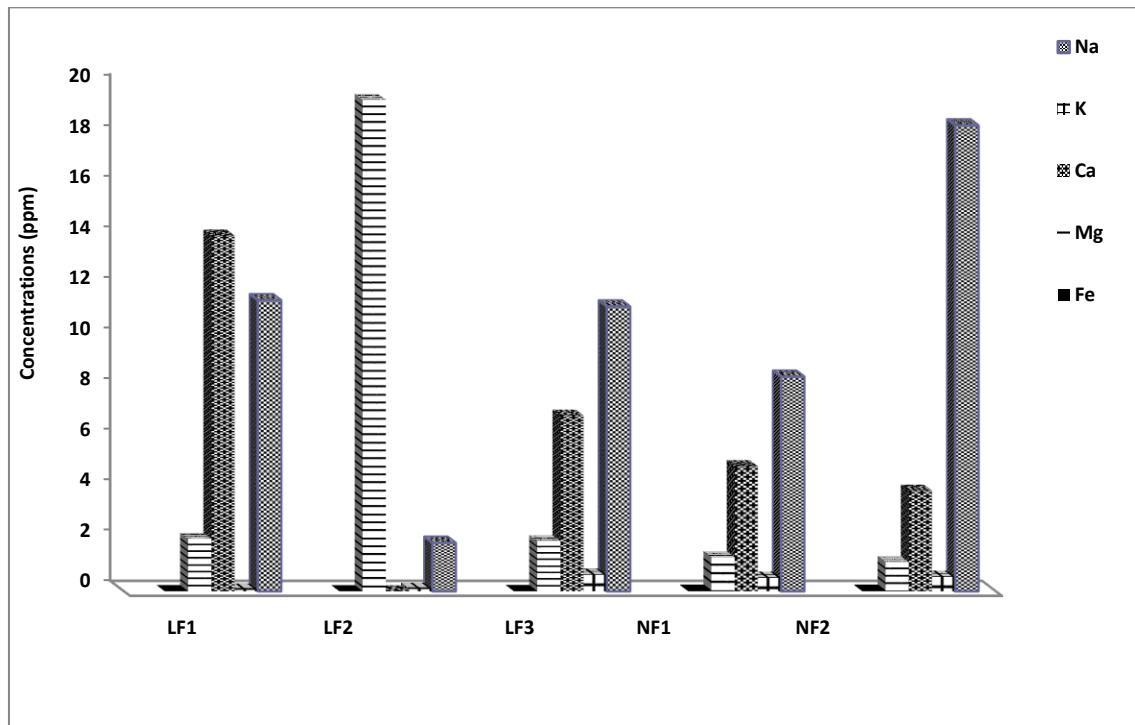
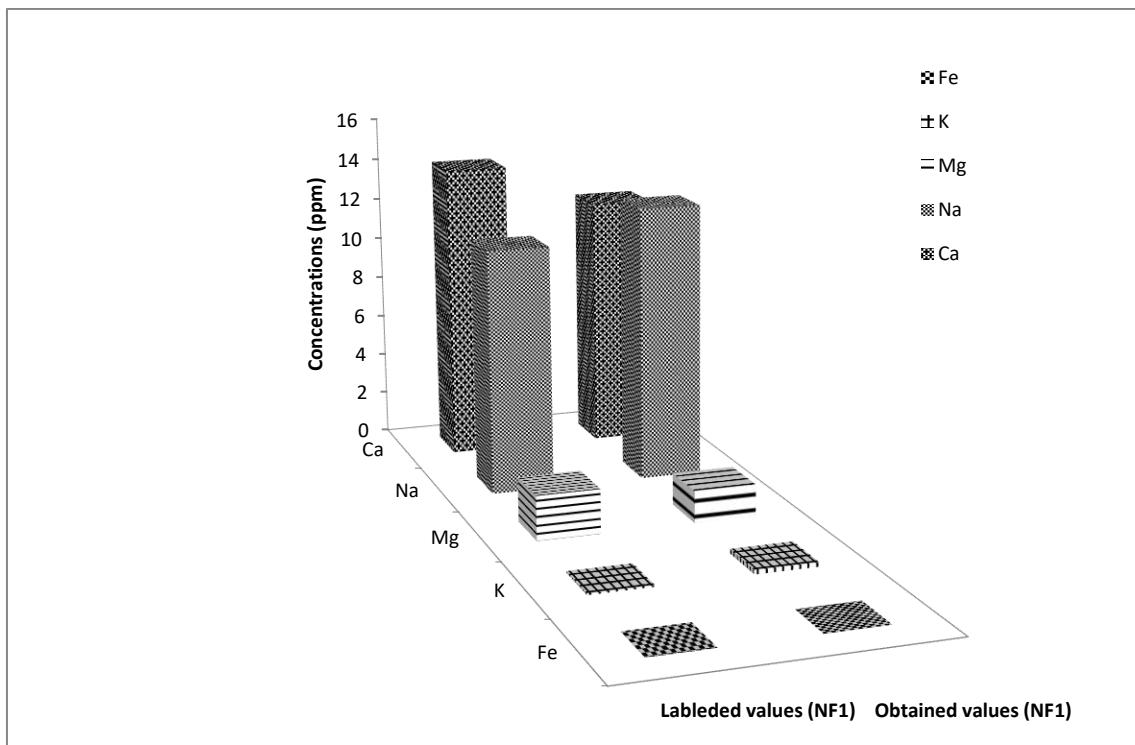
Table 8: Concentration (ppm) of the elements in wells samples

| Element | Concentration (ppm) | | | | | |
|---------|--------------------------|-------------|-------------|---------------|--------------|----------------|
| | Wells samples | | | | | |
| 1 | 2 | 3 | 4 | 5 | 6 | |
| Na | 56.884±0.50 ^a | 41.22±0.86 | 64.03±1.70 | 473.195±20.42 | 78.304±2.96 | 1586.940±75.04 |
| K | 3.53±0.04 | 3.28±0.03 | 3.52±0.10 | 21.363±0.89 | 5.587±0.16 | 12.828±0.348 |
| Ca | 61.24±0.51 | 40.59±1.05 | 69.81±0.18 | 372.129±26.72 | 136.44±11.17 | 1281.293±61.95 |
| Mg | 20.19±1.68 | 8.56±0.56 | 18.68±0.24 | 149.579±5.08 | 35.536±1.44 | 692.615±10.75 |
| Fe | 0.021±0.0003 | 0.038±0.001 | 0.048±0.002 | 0.03±0.001 | 0.032±0.000 | 0.045±0.005 |
| Zn | 0.030±0.003 | 0.031±0.003 | 0.020±0.002 | ND | ND | ND |
| B | 0.333±0.03 | 0.950±0.10 | 0.560±0.02 | 2.000±0.04 | 0.747±0.03 | 2.765±0.09 |
| Al | 0.123±0.01 | 0.148±0.001 | 0.123±0.01 | 0.181±0.02 | 0.182±0.02 | 0.179±0.01 |
| Pb | ND | ND | ND | ND | ND | 0.015±0.001 |
| Cd | ND | ND | ND | 0.002±0.000 | ND | 0.013±0.000 |
| As | ND | ND | ND | ND | ND | 0.032±0.000 |
| Sr | 0.490±0.005 | 0.335±0.006 | 0.585±0.010 | 3.683±0.14 | 0.808±0.03 | 18.794±1.01 |

a: a mean value ± standard deviation (n=3), ND= not detected

Table 9: The correlation coefficient between Mg, Ca and Sr

| Elements | Correlation coefficient | |
|----------|-------------------------|---------------|
| | Factories samples | Wells samples |
| Mg , Ca | -0.6154 | 0.9979 |
| Mg , Sr | -0.5601 | 0.9997 |
| Ca , Sr | -0.0159 | 0.9961 |

**Figure 1:** Concentrations (ppm) of some TEs of different local factories**Figure 2:** Comparisons of the obtained and labeled (NF1) values for some TEs

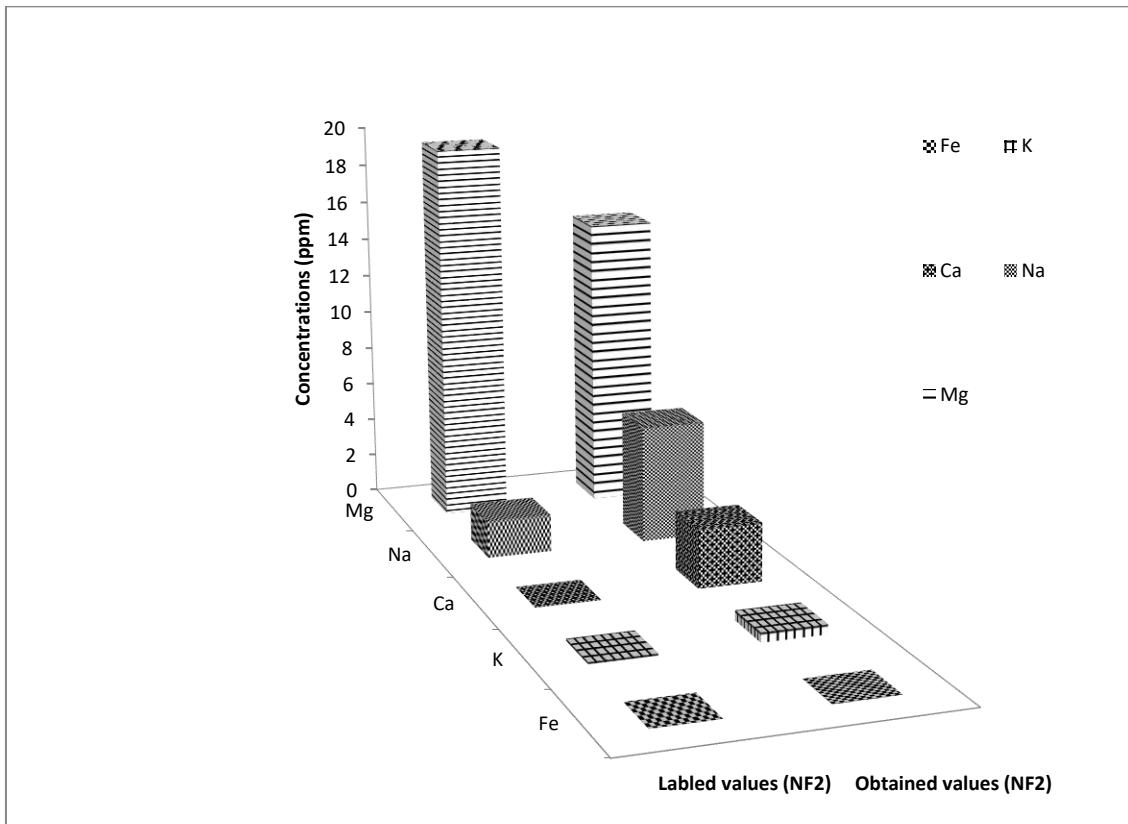


Figure 3: Comparisons of the obtained and labeled (NF2) values for some TEs

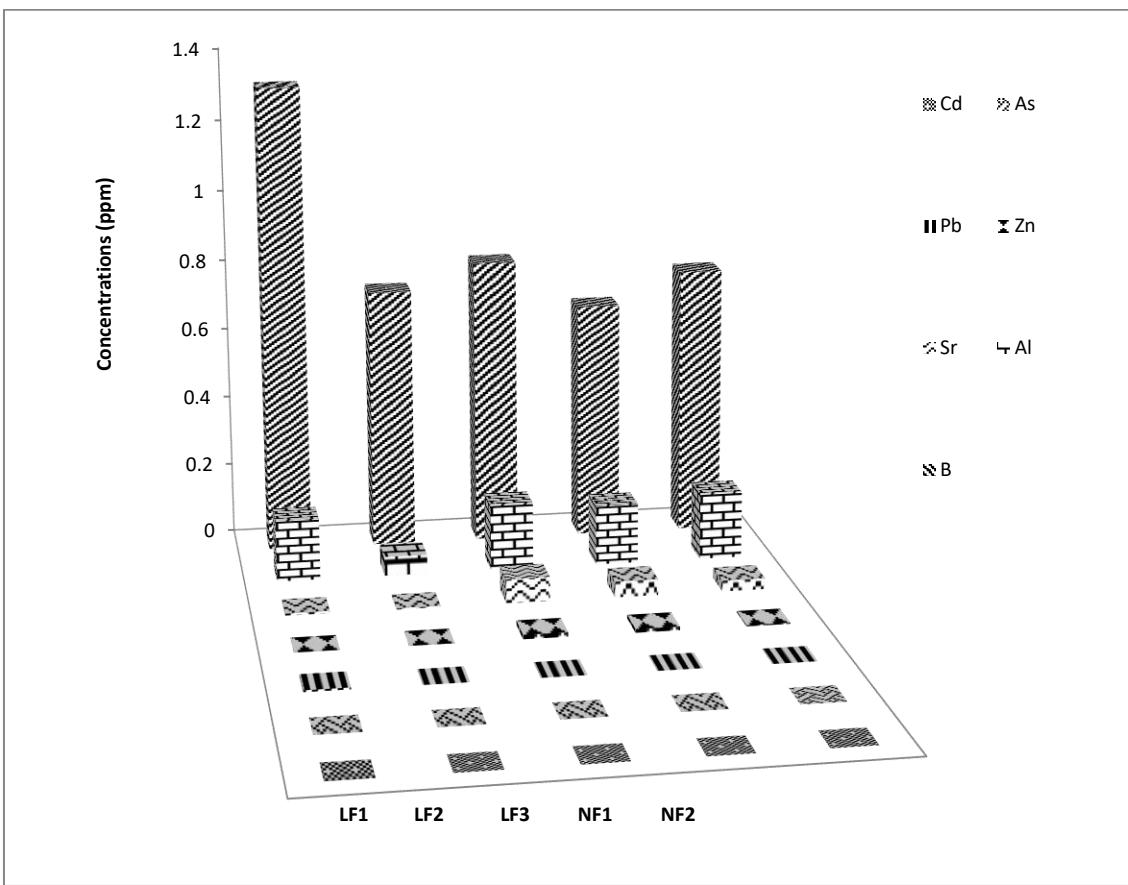


Figure 4: Comparisons of some TEs values of different national and local factories

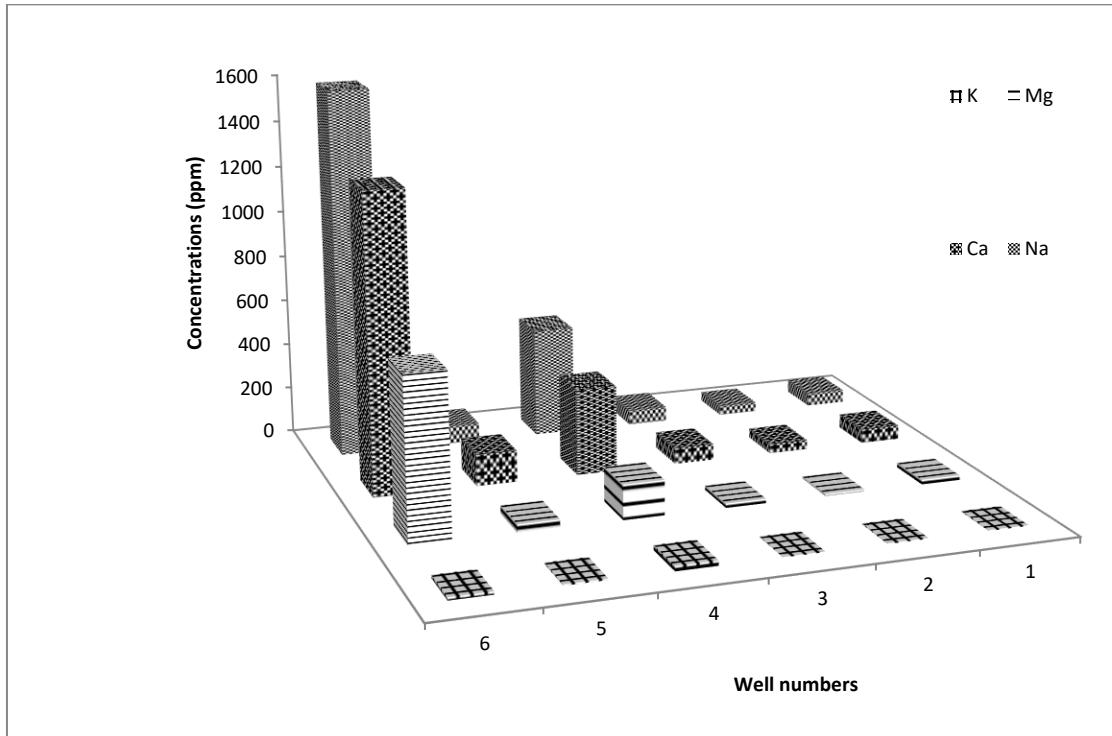


Figure 5: Concentrations (ppm) of some TEs of well samples

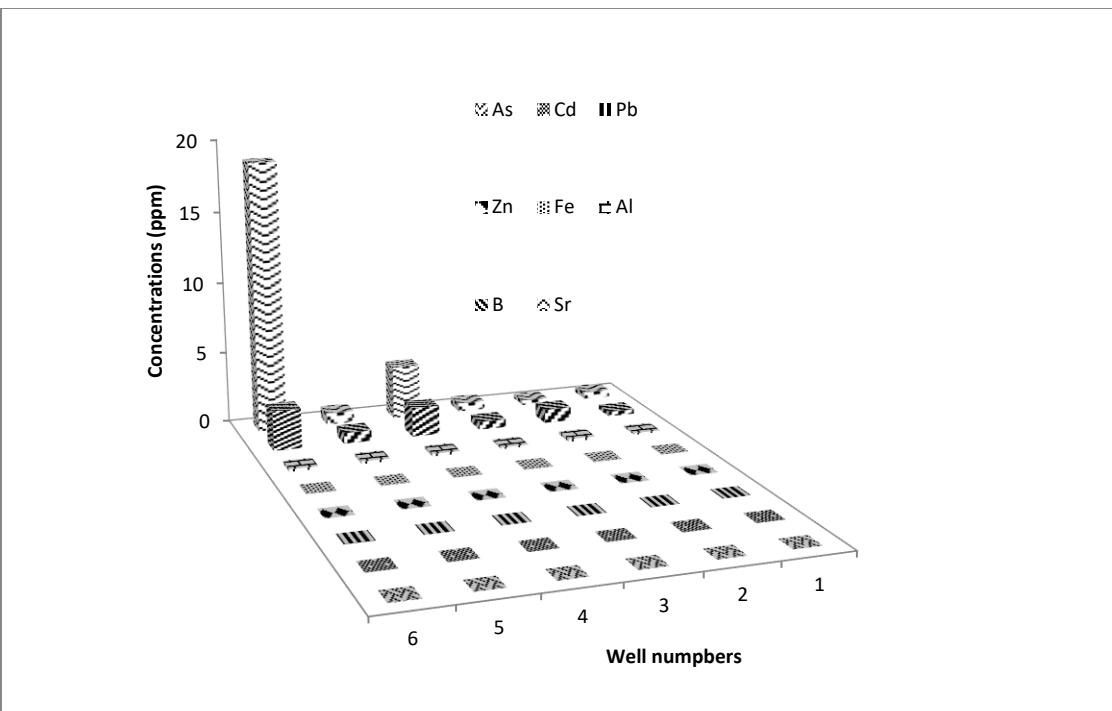


Figure 6: Concentrations (ppm)

4. Conclusions

Determination of TEs in water consumed by human being is important. In this study the TEs in consuming water resources in Turabah Province, Taif Area, KSA was determined. The pre-concentration ten times for factories samples and two times for the well samples and work described in the methodology is a fast, cheap, sensitive

and reliable procedure for TEs analyses in the range of the drinking water and wells water using high resolution ICP-OES.

According to the TEs under study, LOD and drinking water guide line recommended by WHO and SASO, the results obtained of TEs of the local and national factories samples are below the maximum level recommended by

WHO and SASO except B which in a few samples is above the maximum level recommended by SASO. Moreover the results obtained of the some wells samples of TEs Na, K, Ca and Mg are above the maximum level recommended by both WHO and SASO. Strontium was detected in all samples, so intensive study on its toxicity and formula is recommended.

Acknowledgement

The authors gratefully thank the dean of the Deanship of Scientific Research, Taif University, Saudi Arabia, for sponsoring this project. Also, we acknowledge all the individuals who kindly participated in the study including the staff of CPL, Ministry of Petroleum, Khartoum, Sudan, for samples processing.

References

- [1]. Zubair, A. and Farooq, M. A. and Abbasi, H. N., (2008), Toxic and Trace Element Pollution in Storm Water of Karachi: A Graphical Approach. *The Pacific Journal of Science and Technology*, 9, 1, 238-253.
- [2]. Hussain J., Shah, J., Khan K., Lopes A. W., Souza, R. C., Silva J. D.S., Junior E. P. Q. and Nascimento I. A., (2012), Determination of Trace Elements in the Drinking Water of Mardan District KPK, Pakistan. *American-Eurasian J. Agric.& Environ. Sci.*, 12(8).1091-1094.
- [3]. Nadica T, Irina K, Sonja A, Traje S., (2003), Electrothermal atomic absorption spectrometric determination of cobalt in human serum and urine. *Acta Pharm.* 53: 83-90.
- [4]. Afridi I., Kazi G., Sirajuddin N., Kandhro G., Baig J., Shah A., Jamali K., Arain M., Wadhwa S., Khan S., Kolachi N., Shah F., (2011), Chromium and Manganese Levels in Biological Samples of Pakistani Myocardial Infarction Patients at Different Stages as Related to Controls. *Biol. Trace Elem Res* 142: 259-273.
- [5]. Forrer R., Gautschi K., Lutz H., (2001), Simultaneous Measurement of the Trace Elements Al, As, B, Be, Cd, Co, Cu, Fe, Li, Mn, Mo, Ni, Rb, Se, Sr, and Zn in Human Serum and their Reference Ranges by ICP-MS. *Biol. Trace Elem Res* 80: 77-93.
- [6]. Momen A. A., Khalid M. A., Elsheikh M.A., Hag Ali D., M., (2013), Assessment and modifications of digestion procedures to determine trace elements in urine of hypertensive and diabetes mellitus patients. *J Health Spec*, 1, 122-8.
- [7]. Momen A. A. and Lilly B. E., (2010), Trace Elements in Smoker's and Non-Smoker's Urine Samples, *Juba University J. Ar. and Sci.*, 9, 27-40.
- [8]. World Health Organization (WHO), Environmental Health Criteria, 3, Geneva, Switzerland, (1977).
- [9] World Health Organization (WHO), Environmental Health Criteria, *Tech. Rep. Ser.* 647 , Geneva, Switzerland, (1980).
- [10]. WHO. Geneva, Trace elements in human nutrition and health, WHO Library Cataloguing in Publication Data, ISBN 92 4 156173 4 (NLM Classification: QU 130), (1996).
- [11]. He FJ, MacGregor GA. (2008) Beneficial effects of potassium on human health, *Physiol Plant*, 133(4):725-35.
- [12]. WHO. Geneva, Calcium and magnesium in drinking-water. Report of a WHO expert committee, 1 -135, (2009).
- [13]. Khun N.W. and Liu E., (2009), Linear sweep anodic stripping voltammetry of heavy metals from nitrogen doped tetrahedral amorphous carbon thin films. *Electrochimica Acta*, 54,2890-2898.
- [14]. WHO. Geneva, International Programme on Chemical Safety, Aluminium, *Environ. Health Criteria* 194, (1997).
- [15]. Smedley, P. L. and Kinniburgh D. G., (2002), Behaviour and distribution of Arsenic in natural waters, *Appl. Geochemistry*, 17, 517-568.
- [16]. Plant J. A., Arsenic and Selenium, in: H. D. Holland and K. K. Elsevier, Turekian (Eds.) *Environ. Geochemistry, Treaties in Geochemistry*, 9, (2003)
- [17]. National Research Council. Arsenic in Drinking Water. National Academy Press, Washington DC, (1999).
- [18]. Maroof F.B.A. , Hadi , D.A., Khan A.H. and Chowdhury , A. H., (1986) Cadmium and Zinc concentrations in drinking water supplies of Dhaka city, *Bangladesh. Sci. Total Environ.*, 53, 233 – 238.
- [19]. Maroof F.B.A., Hadi , D.A., Khan , H.A. and Chowdhury , A.H., (1990), Cadmium and Zinc levels of drinking water supplies in some major cities of Bangladesh . *Nucl. Sci. and Appl.* 2, 77 – 80.
- [20]. Ling-W. X., Shao-X. L., Ji-Wen J., Xia-J. and Jian L., (1988), Trace elements in Medicine, *Brit. J. Ind. Med.* 50 , 93-96.
- [21]. Nogawa K., Kobayashi E. and Honda R. A., (1979), Study of the relationship between cadmium concentrations in urine and renal effects of cadmium. *Environ. Health Perspectives*, 28, 161-168.
- [22]. International Agency for Research on Cancer, (IARC) Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Supplement No. 7, 230-232, (1987).
- [23]. Forrest H. Nielsen, (1997), Boron in human and animal nutrition, *Plant and Soil*, 193, 1-2, 199-208.
- [24]. Nielsen, s. pores,(2004),The biological role of strontium, *Bone*,35, 3, 583-588.
- [25]. Fassel V.A., (1976) Simultaneous Determination of Wear Metals in Lubricating Oils by Inductively-Coupled Plasma Atomic Emission Spectrometry. *Anal.Chem.* 48,516-519.
- [26]. Merryfield R.N. and Loyd R.C., (1979), Simultaneous Determination of Metals in Oil by Inductively Coupled Plasma Emission Spectrometry. *Anal. Chem.* 51, 1965-1968.
- [27]. Elgorashe R. , Idris A., Malik A. Abdelrahman and Saeed A., (2014), Facile Assay Method for Norfloxacin and Ciprofloxacin by Sequential Injection Chromatography, *ActaChromatography*, 26(2): 321 – 334.
- [28]. M. Thompson, S.L.R. Ellison, and R. Wood, (2002), *Pure Appl. Chem.*, 74, 835.
- [29]. U.S. Environmental Protection Agency. Method 200.7: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, page 27 revision 4.4, Version EMMC (1994).
- [30]. Zahid W. M. (2003) "Quality of Local and Imported Bottled Water in Saudi Arabia" *Journal of King Abdulaziz University-Engineering Sciences* (in Arabic), 14, 2,81.
- [31]. Stringfield, V. T., (1966), Artesian Water in Tertiary Limestone in the Southeastern State, Geological survey professional paper 517, United states Government printing office, Washington, pp. 138 – 139.