Full Length Research Paper

Determination of common cations and ammonium by ion chromatography in water samples of Baghdad city part.2

Hassan M Alsudani*, Redha I. Al-Bayati ,Mahmood M. Barbooti*** ,Abdul Amir Hassan Kadhum**** and Farhani Shamsudin*****

*Ibn- ALBittar / SDI Co. / the Ministry of Industrial
**DEPT.CHEMISTRY- COLLEGE OF SCIENCE- ALMUSTANSIRIYA UNIVERSITY
*** TECHNOLOGY – UNIVERSITY / SCHOOL OF APPLIED SCIENCES.
**** Department of Chemical and process Engineering
***** Sales Engineer, Metrohm, Malaysia, Sdn. Bhd

Determination of common cations by IC methods in Baghdad was carried out in this investigation. The optimum values of the instrumental parameters were reached best in relative standard deviation (RSD), correlation coefficient (r2) and method detection limits (MDLs) and other parameters to approving the precision and accuracy of this method. Both peak height (PH) and peak area (PA) were used for the evaluation of the IC signals. All standards and samples have been prepared by ultra pure water. Generally the peaks for cations were clearly, good resolution and there are no any interaction between its. We recorded the total time for cation analyses was about 15.5 mins.The elution of cations follows the order: Li+, Na+, NH4+, K+, Ca2+ and Mg2+ that because for cation separation the cation-exchange resin is usually a sulfonic acid group.

Keyword: Chromatography, ammonium, water samples, Baghdad city and cations .

INTRODUCTION

A whole variety of chemicals from industry, such as metals and solvents, and even chemicals which are formed from the breakdown of natural wastes (ammonia, for instance) are poisonous to fish and other aquatic life. Pesticides used in agriculture and weeds-- are another type of toxic chemical. Some of these can accumulate in fish and shellfish and poison people, animals, and birds that eat them. Materials like detergents and oils float and spoil the appearance of a water body, as well as being toxic; and many chemical pollutants have unpleasant odors. The Niagara River, between the US and Canada, even caught fire at one time because of flammable chemical wastes discharged into the water. (Fritz et al 2009 and Ainsworth 2004) Chemicals can enter water ways from a point source or a non point source.

Point sourcepollution is due to discharges from a single source, such as an industrial site. Nonpoint-source pollution involves many small sources that combine to cause significant pollution. For instance, the movement of rain or irrigation water over land picks up pollutants such as fertilizers, herbicides, and insecticides and carries them into rivers, lakes, reservoirs, coastal waters, or groundwater. Another non point source is storm water that collects on roads and eventually reaches rivers or Paper and pulp mills consume large volumes of water and discharge liquid and solid waste products into the environment. The liquid waste is usually high in biological oxygen demand, suspended solids, and chlorinated organic compounds such as dioxins. (Koller et al 2000 and Omar 2000)

The storage and transport of the resulting solid waste (wastewater treatment sludge, lime sludge, and ash) may also contaminate surface waters. Sugar mills are

* Corresponding Author Email : Hassan_nsr2001@Yahoo.com

associated with effluent characterized by biological oxygen demand and suspended solids, and the effluent is high in ammonium content. In addition, the sugarcane rinse liquid may contain pesticide residues. Leather tanneries produce a significant amount of solid waste, including hide, hair, and sludge. The wastewater contains chromium, acids, sulfides, and chlorides. Textile and dye industries emit a liquid effluent that contains toxic residues from the cleaning of equipment. Waste from petrochemical manufacturing plants contains suspended solids, oils and grease, phenols, and benzene. Solid waste generated by petrochemical processes contains spent caustic and other hazardous chemicals implicated in cancer. (Ainsworth 2004, Doust et al 1994 and Nollet 2007)

Some pesticides are applied directly on soil to kill pests in the soil or on the ground. This practice can create seepage to groundwater or runoff to surface waters. Some pesticides are applied to plants by spraying from a distance—even from airplanes. This practice can create spray drift when the wind carries the materials to nearby waterways. Efforts to reduce the use of the most toxic and long-lasting pesticides in industrial countries have largely been successful, but the rules for their use in developing countries may be more permissive, and the rules of application may not be known or enforced. Hence, health risks from pesticide water pollution are higher in such countries. (Ahmed and Ali 2000 and Kahlown et al 2004)

Chromatography is a separation method based on the affinity difference between two phases, the stationary and mobile phases. A sample is injected into a column, either packed or coated with the stationary phase, and separated by the mobile phase based on the difference in interaction (distribution or adsorption) between compounds and the stationary phase. Compounds with a low affinity for the stationary phase move more quickly through the column and elute earlier. The compounds that elute from the end of the column are determined by a suitable detector. In ion chromatography, an ion exchanger is used as the stationary phase, and the eluent for determination of anions is typically a dilute solution of sodium hydrogen carbonate and sodium carbonate. Colorimetric, electrometric or titrimetric detectors can be used for determining individual anions. In suppressed ion chromatography, anions are converted to their highly conductive acid forms; in the carbonate–bicarbonate eluent, anions are converted to weakly conductive carbonic acid. The separated acid forms are measured by conductivity and identified on the basis of retention time as compared with their standards. (Fritz et al 2009 and Gunzler and Williams 2001).

The study of chemical pollutants in various types of water in Baghdad city were found necessary in order to investigate all of surrounding factors affecting on water pollution, so, the present study aimed to establishment of ion chromatographic method for drinking and raw water quality monitoring.

THE INTERFERENCES OF CATIONS ANALYSIS

1. High concentration of analyte, cations can interfere with the determination of low concentrations of other analyte cations with similar retention times. For instance, high levels of sodium can interfere with the determination of low levels of ammonium (that is, at ratios >1000:1) (1).
In method present don't occurred same these interferences because of all samples diluted to five times to prevent these interferences.
2. Sodium is a common contaminant from many sources such as fingers, water, detergents, glassware, and other incidental sources. As a precaution, the user of the method is advised to wear plastic gloves and use plastic ware for all solutions, standards, and prepared samples. In addition, method blanks should be monitored for background sodium contamination (Weiss 2004).
3. High levels of sample acidity, that is, low pH, can also interfere with this analysis by overloading that column, leading to poor peak shape and loss of resolution. The pH at which the chromatograph separation begins to exhibit poor peak shape depends upon the ion- exchange capacity of the column (Fritz et al 2009 and Weiss 2004).
To reduce or remove this interference by adjust pH of all samples (2-2.5).

Experimental design

The practical part in method present according to (ASTM 2008, Kolb and Seabert 2002).

Sampling

Water samples were collected from various locations (table-1) from August and September (2008).
HPIC Technique:
The HPIC measurements were carried out on a Compact high-performance ion chromatography, 761 Compact IC system supplied from Metrohm, Switzerland, (P.N. 6.2620.110) (14). The system is connected to a PC-controller; Rapid start – click and analog output for connection to external data systems without chemical suppression.
For automation tasks, the system is equipped with 766 IC Sample Processor, the 788 IC Filtration Sample Processor; the 788 IC Dialysis Sample Processor the Metrohm 761 Compact IC system is characterized by:
- Built-in 6-way injection valve;
- Low-pulsation double piston pump, flow range 0.2 to 2.5 ml/min, maximum pressure 25 MPa (250 bar, 3625 PSI);
- Pulsation dampener;
- Insulated column compartment;
- Detector temperature-stabilized to better than 0.01 °C, temperature range 25 ... 45 °C in 5 °C steps, three measuring ranges 0 ... 50 µS, 0 ... 250 µS, 0 ... 1000 µS

RESULTS AND DISCUSSION

All standards and samples solutions have been prepared by UPW. Figure.1
Figure. (2 to 7) show the calibration curves of cations:-
The precision of the determination was evaluated by

Table (1): various types of water collected from various studied location in Baghdad city.

NO.	TYPE OF WATER	NO. OF SAMPLES	LOCATION
1	DRINKING WATER (DWET)	22	EAST TIGRIS PLANT
2	RIVER WATER (RWW)	22	WATHBA PLANT
3	DRINKING WATER (DWW)	22	WATHBA PLANT

Table (2): Represent analytical performance parameters of a single cation standard.

Cation	Peak No.	RT (min)	Range (mg/L)	Linearity (r^2)	MDL (mg/L)	(%RSD) Concs.
Lithium	1	2.99**	0.02 -50	0.99999	0.01*	3.615*
Sodium	2	3.66	0.2 - 250	0.99930	0.02	4.939
Ammonium	3	4.08	0.03 - 50	0.99888	0.02	6.928
Potassium	4	5.28	0.2 - 50	0.99707	0.12	8.112
Calcium	5	11.62	0.2 - 50	0.99988	0.09	6.451
Magnesium	6	15.46	0.2 - 150	0.99970	0.15	5.773

*: **P** Value <0.05, **: **P** Value <0.01
The values in table (1) were compatible with [15, 18, and 19] and no compatible with [20, 21].
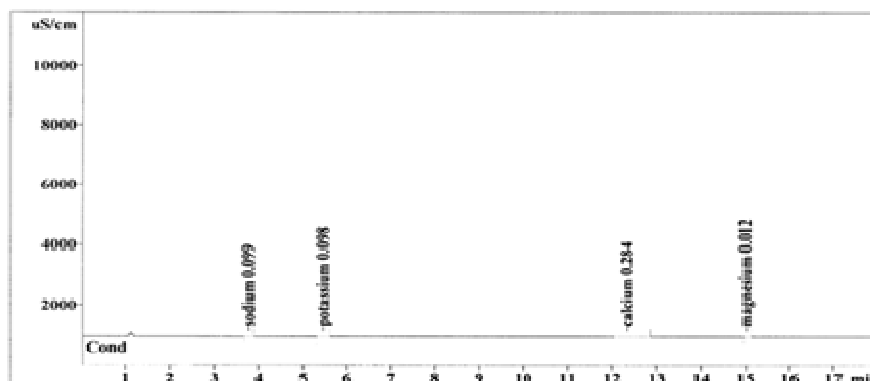
Figure 1 – Chromatogram of cations in UPW where y- axis represents PH in µs/cm and x- axis represents time in (min).

running IC (under chromatographic conditions) for above calibration curves of six cations, for seven replicate of each standard cations and recorded the analytical parameters in table (1).

Standardization curve to combination cation analyses

One of the advantages of IC method is the possibility of determining combination cations in a single run with keep

the precision at high levels (168,178). The general shapes of the chromatograms by using (2, 5 and 10 ppm) are show in Figure. (8, 9 and 10) respectively.

Determination of cations in water samples for DWET, RWW, and DWW in Baghdad city

The figures (11 to 13) illustrated the results of cation determine by IC technique under analytical conditions
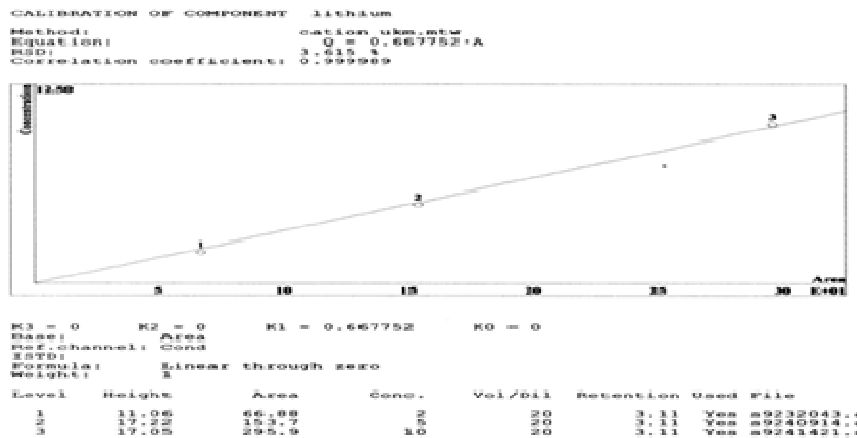
CALIBRATION OF COMPONENT   lithium

Method: cation ukm.mtw
Equation: Q = 0.667752*A
RSD: 3.615 %
Correlation coefficient: 0.999989

K3 = 0   K2 = 0   K1 = 0.667752   K0 = 0
Base: Area
Ref.channel: Cond
ISTD:
Formula: Linear through zero
Weight: 1

Level	Height	Area	Conc.	Vol/Dil	Retention	Used	File
1	11.06	66.88	2	20	3.11	Yes	a9232043.c
2	17.22	153.7	5	20	3.11	Yes	a9240914.c
3	17.05	295.9	10	20	3.11	Yes	a9241421.c

Figure (2) - Calibration curve of Lithium where y- axis represents Conc. of Lithium in ppm (mg/L) and x- axis represents PA /10 in μs/cm.sec.

CALIBRATION OF COMPONENT   sodium

Method: cation ukm.mtw
Equation: Q = 2.48901*A
RSD: 1.010 %
Correlation coefficient: 0.999301

K3 = 0   K2 = 0   K1 = 2.48901   K0 = 0
Base: Area
Ref.channel: Cond
ISTD:
Formula: Linear through zero
Weight: 1

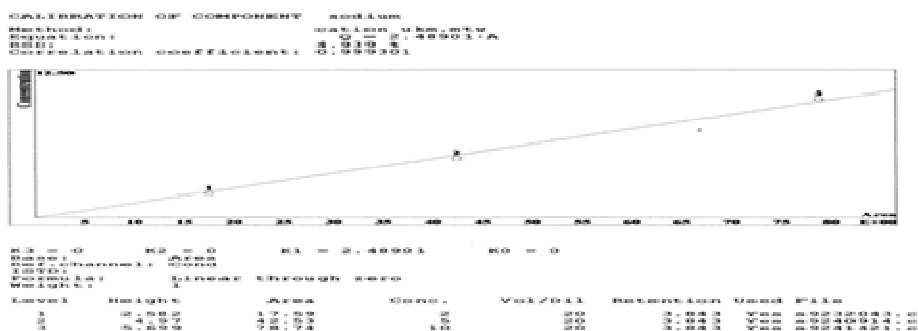| Level	Height	Area	Conc.	Vol/Dil	Retention	Used	File
1	2.552	17.55	2	20	3.83	Yes	a9232091.d
2	4.57	43.53	5	20	3.83	Yes	a9240914.d
3	6.455	78.74	10	20	3.83	Yes	a9241421.d

Figure (3) - Calibration curve of Sodium where y- axis represents Conc. of Sodium in ppm (mg/L) and x- axis represents PA /10 in μs/cm.sec.

CALIBRATION OF COMPONENT   ammonium

Method: cation ukm.mtw
Equation: Q = 2.37641*A
RSD: 5.028 %
Correlation coefficient: 0.998650

K3 = 0   K2 = 0   K1 = 2.37641   K0 = 0
Base: Area
Ref.channel: Cond
ISTD:
Formula: Linear through zero
Weight: 1

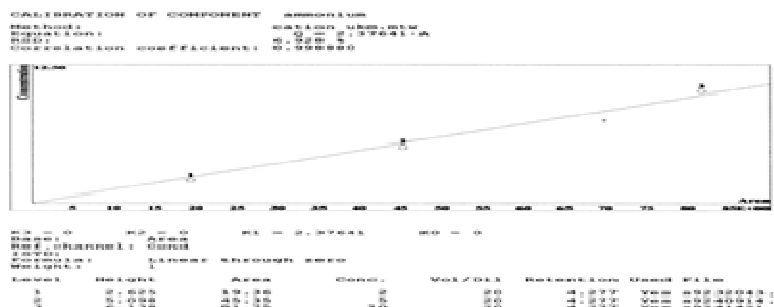| Level	Height	Area	Conc.	Vol/Dil	Retention	Used	File
1	2.525	19.35	2	20	4.377	Yes	a9232091.c
2	5.044	45.95	5	20	4.377	Yes	a9240914.c
3	6.155	45.75	10	20			

 Figure (4) - Calibration curve of Ammonium where y- axis represents Conc. of Ammonium in ppm (mg/L) and x- axis represents PA /10 in μs/cm.sec.

that show in figure. (13) for various studied locations as shown in table 2.
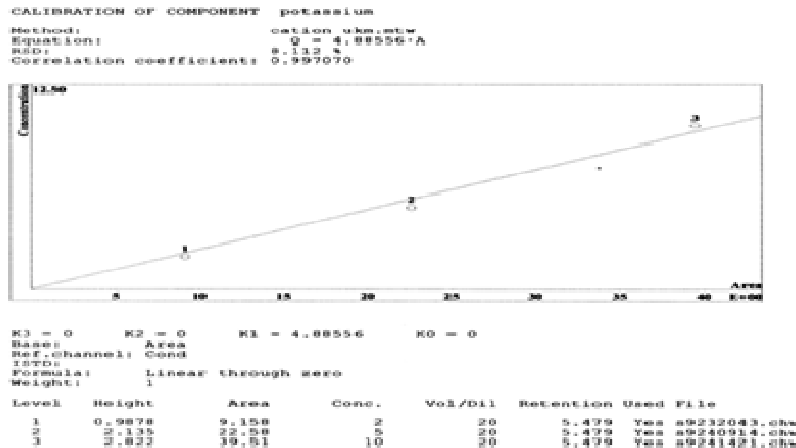
Lithium

Not detect in DWET, RWW and DWW.

```
CALIBRATION OF COMPONENT  potassium
Method:                    cation ukm.mtw
Equation:                  Q = 4.80556*A
RSD:                       8.112 %
Correlation coefficient:   0.997070
```



```
K3 = 0      K2 = 0      K1 = 4.80556      K0 = 0
Base:            Area
Ref.channel:  Cond
ISTD:
Formula:      Linear through zero
Weight:       1

Level    Height       Area        Conc.     Vol/Dil   Retention  Used  File
  1      0.9878       9.158         2          20       5.479     Yes   a9232043.chm
  2      2.135       22.58          5          20       5.479     Yes   a9240914.chm
  3      2.822       38.51         10          20       5.479     Yes   a9241421.chm
```

Figure (5) - Calibration curve of Potassium where y- axis represents Conc. of Potassium in ppm (mg/L) and x- axis represents PA /10 in µs/cm.sec.

```
CALIBRATION OF COMPONENT  calcium
Method:                    cation ukm.mtw
Equation:                  Q = 2.68077*A
RSD:                       6.451 %
Correlation coefficient:   0.999877
```



```
K3 = 0      K2 = 0      K1 = 2.68077      K0 = 0
Base:            Area
Ref.channel:  Cond
ISTD:
Formula:      Linear through zero
Weight:       1

Level    Height       Area        Conc.     Vol/Dil   Retention  Used  File
  1      0.6946      18.49          2          20      12.55      Yes   a9232043.c
  2      1.334       38.25          5          20      12.55      Yes   a9240914.c
  3      1.596       73.21         10          20      12.55      Yes   a9241421.c
```
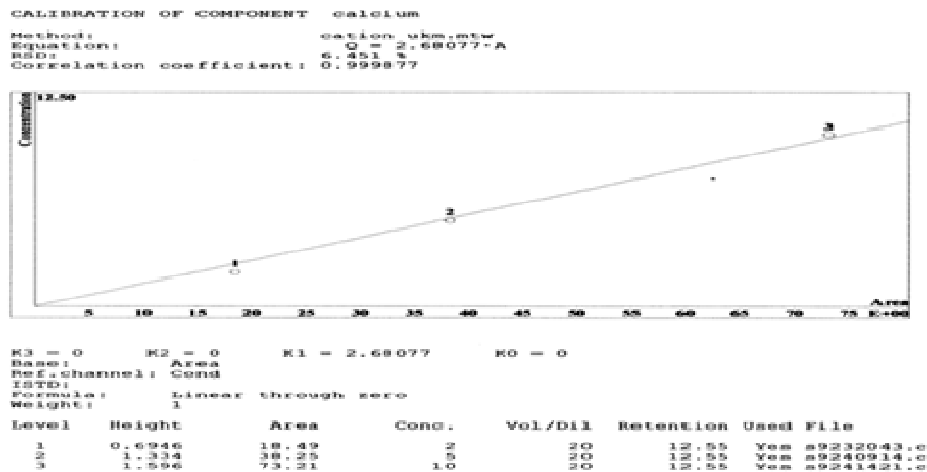
Figure (6) - Calibration curve of Calcium where y- axis represents Conc. of Calcium in ppm (mg/L) and x- axis represents PA /10 in µs/cm.sec.

Sodium

The concentration average of Sodium determines by IC in various locations of August and September, 2008 was as follow:
DWET: 32.5 mg/L
RWW: 35.0 mg/L
DWW: 38.0 mg/L
According to our results, we conclude that water after treatment (DWW) was highly than that before treatment (RWW), that's because, addition of Sodium Compound through water treatment. And Sodium concentrations in DW were always in Wathba plant highly than East Tigris plant due to the Wathba plant located in the center of Baghdad city while, the East Tigris plant located around Baghdad city, therefore Wathba plant was highly eradicated to contamination than East Tigris plant.
All of these concs. of Sodium were within the limits of standards according to (WHO vol. 1(2006) and IQS/417/ 2001).

Ammonium

Ammonium was present in DWET, DWW in following average of August and September, 2008:
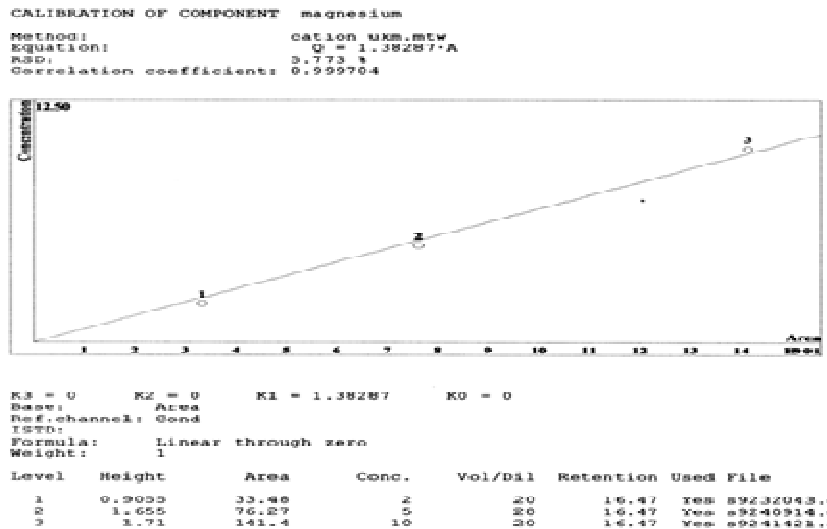DWET: 0.21 mg/L

```
CALIBRATION OF COMPONENT  magnesium

Method:                      cation ukm.mtw
Equation:                    Q = 1.38287·A
RSD:                         3.773 %
Correlation coefficient:     0.999704
```



```
K3 = 0        K2 = 0        K1 = 1.38287        K0 = 0
Base:            Area
Ref.channel:     Cond
ISTD:
Formula:         Linear through zero
Weight:          1

Level    Height      Area      Conc.    Vol/Dil   Retention Used File
  1      0.9033      33.40       2         20       16.47    Yes  s9232043.c
  2      1.655       76.27       5         20       16.47    Yes  s9240914.u
  3      1.71        141.4      10         30       16.47    Yes  s9241421.c
```

Figure (7) - Calibration curve of Magnesium where y- axis represents Conc. of Magnesium in ppm (mg/L) and x- axis represents PA /10 in µs/cm.sec.
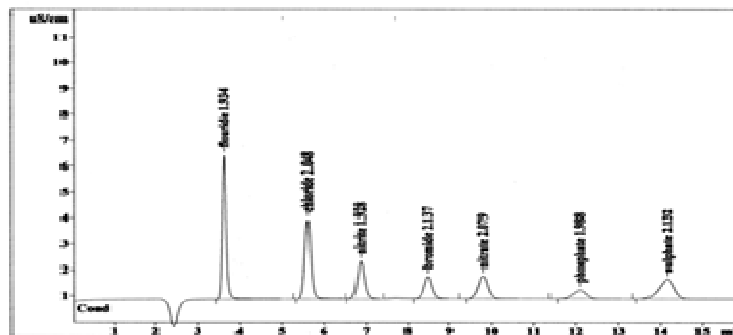
Figure (8) – Chromatogram of combination cations standard for concentration 2 ppm.

DWW: 0.19 mg/L

The concentrations of ammonium were highly than the standard limits according to (WHO vol. 1(2006) and IQS/417/ 2001) in water samples for DWET and DWW plants. That's because of insufficient of water transport system from plant to houses, passage through the contaminated small swamps and creeks with human disposals.Wheares the ammonium not detected in RWW due to don't available the factors above.

Potassium

The average of Potassium concentration determine by IC in various locations of August and September (2008) was as follow:
DWET: 1.75 mg/L
RWW: 2.0 mg/L

DWW: 4.5 mg/L

According to our results, we conclude that water after treatment (DWW) was highly than that before treatment (RWW), that's because, addition of Potassium Compounds through water treatment. And Potassium concentrations in DW were always in Wathba plant highly than East Tigris plant due to the same reason describe in sodium. All of these concs. of Pot. Were within the limits of standards according to (WHO vol. 1(2006) and IQS/417/ 2001).

Calcium

The concentration average of calcium determines by IC in various locations for August and September, 2008 was as follow:
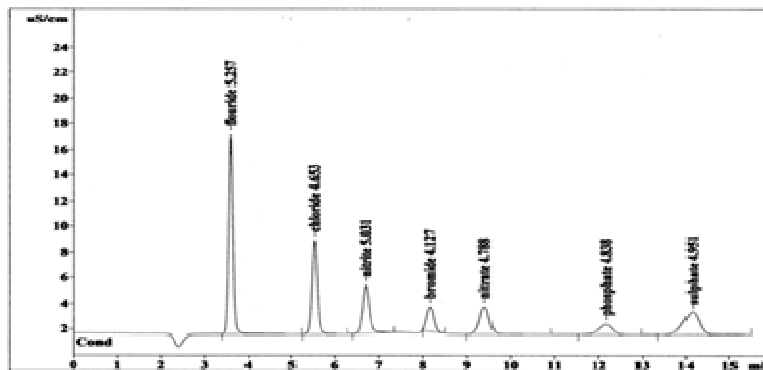DWET: 101.5 mg/L

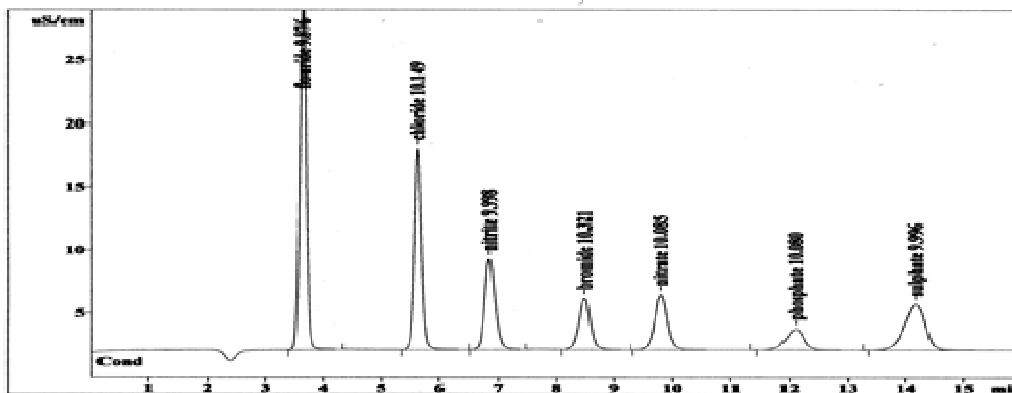Figure (9) – Chromatogram of combination cations standard for concentration 5 ppm.

Figure (10) – Chromatogram of combination cations standard for concentration 10 ppm.
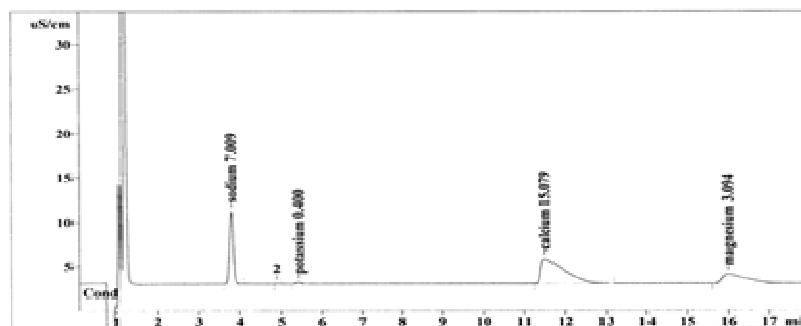

Figure (11)-Chromatogram of cations in raw water sample for Wathba plant (5 x dilutions).

RWW: 142.5mg/L
DWW: 145.0 mg/L

Calcium concentrations in DW were always in Wathba plant highly than East Tigris plant due to the same reason describes in sodium.
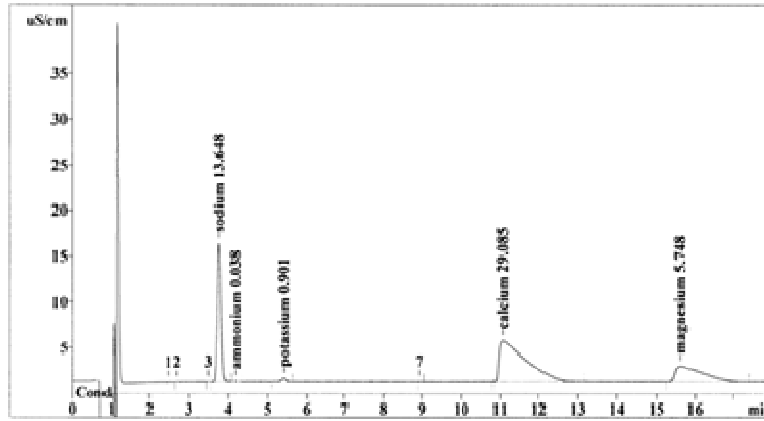
Figure (12) - Chromatogram of cations in drinking water sample for Wathba plant (5 x dilutions).

Report date: 9/26/2008 2:59:58 PM
Printed by: Metrohm (M) Sdn Bhd

Ident: cat 2 dil
Analysis from: 9/24/2008 10:52:49 AM
File: s9241052.chw   Last save: 9/26/2008 2:05:16 PM

Method: cation ukm.mtw   Last save: 9/23/2008 9:02:18 PM
Run operator: metrohm
Analysis number: 1851

SAMPLE: C4
  :   new eluent- tartaric +dipicolonic
Vial number: 1
Volume: 20.0 µL
Dilution: 1.00
Amount: 1.0000

COLUMN: METROSEP C 2 150/4.0 (6.1010.220)
Size: 4.0 x 150 mm
Number:
Part.size: 7.0 µm

ELUENT: 4 mM Tartaric acid
                        0.75 mM dipicolinic acid

Flow: 0.90 mL/min
Temperature: 20.0°C
Pressure: 3.4 MPa
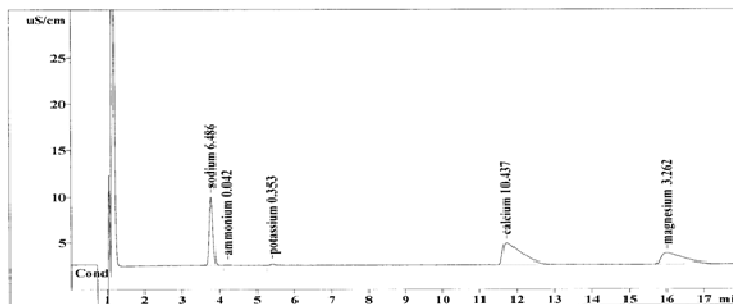
Quantitation method: Custom

No	Retention min	Height uS/cm	Area uS/cm*sec	Conc. mg/L	Name
1	3.78	7.37	52.117	6.486	sodium
2	4.21	0.04	0.350	0.042	ammonium
3	5.42	0.15	1.445	0.353	potassium
4	11.72	2.27	77.866	10.437	calcium
5	16.01	1.12	47.179	3.262	magnesium
5	18.00	10.96	178.957	20.580	

Figure (13) - Chromatogram of cations in drinking water sample for East Tigris plant (5 x dilutions).

All of these concs. of calcium were within the limits of standards according to (WHO vol. 1(2006) and IQS/417/2001).

Magnesium

The concentration average of Magnesium determines by IC in various locations for August and September, 2008 was as follow:
DWET: 16.3 mg/L
RWW: 15.5 mg/L
DWW: 28.7 mg/L
According to our results, we conclude that water after treatment (DW) was highly than that before treatment (RW), that's because, addition of calcium compounds through water treatment. And calcium concentrations were always in Wathba plant highly than East Tigris plant due to the same reasons that describe previously in sodium.
All of these concs. of sodium were within the limits of standards according to (WHO vol. 1(2006) and IQS/417/2001).

REFERENCES

Ainsworth R (2004). Safe piped water: Managing microbial water quality in piped distribution systems. World Health Organization, Geneva.
ASTM (2008) .Annual book of ASTM standards, Standard Practices for Sampling Water from Closed Conduits, D - 3370, vol. 11(1): 1-29.
ASTM. (2003)   Annual book of ASTM standards: test method for determination of dissolved alkali and alkaline earth cations and ammonium in water and wastewater by ion chromatography, D - 6919, vol. 11.01, pp. 1177-1185.
Doust JL, Schmidt M, Doust LL (1994). Biol. Rev. of the Cambridge Philos. Soc. 69, 147–186.
Dionex Co (2004). comparison of suppressed to nonsuppressed conductivity detection for the determination of common inorganic cations, application Note 157. pp. 1-11.
Fritz J S, Gjerde DT (2009). Ion chromatography. 4th ed. Wiely Co. Germany, provide page
Gunzler H, Williams A, Hand book of analytical techniques,   vol. 2, Wiley-VCH, Germany, (2001).
Kahlown MA, Tahir MA, Sheikh AA, Pakistan Council of Research in Water Resources, Islamabad, ISBN: 969-8469-13-3. (2004).
Koller G, gerbu K, Fent K (2000). Envir. Sci. Pollut. Res. 7(3):135–143.
Muhammad A, Lim LW,   Takeuchi T J(2008):   Chromatogr A, 1182:169-175.
. Kolb M, Seabert A (2002).practical ion chromatography. Metrohm Ltd., CH-9101 Herisau, Metrohm catalogue – 761 compact IC, Metrohm Ltd., CH-9101 Herisau, (2001).
Nollet LM(2007). Hand book of water analysis.2nd ed.CRC press.
Ahmed K, Ali W(2000). J. Drainag. and Water Manage. Vol. 4, No. 1&2, (2000).
Omar MA (2000). MSc. Thesis in Environmental Engineering, Institute of Environmental Science and Engineering, National University of Sciences and Technology, Rawalpindi
Weiss   J (2004). Handbook of ion chromatography. 3rd Ed., vol. 2, Wiley-VCH, Germany,
WHO (2006). Guidelines for drinking water quality. Vol.1.
IQS / 417 / 2001.
Gros N Gorenc BJ(1994) Chromatogr. 39(7/8): 448-459.
Dionex Co (2001). determination of inorganic cations and ammonium in environmental waters by ion chromatography using the Ion Pac CS16 column, application Note 141. pp. 1-8.