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Determination of some metals ions concentrations in some Iraqi water resources

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Abstract

In this research a water quality in some Iraqi water resources was studied. A various metal and some ions concentrations were determined in different water resources (tab, river and ground water). The results included the determination of Ca^{++}, Mg^{++}, Cl^{-}, Cu^{++}, Fe, and finely Pb ion concentrations. The calcium concentration was in the range (20.73 to 44.66) ppm, (39.19 to 73.19) ppm and (32.42 to 58.79) ppm in tap, river and ground water samples, respectively. Copper concentration was in the range (0.053 to 0.105), (0.036 to 0.069) and (0.035 to .058) ppm in tap, river and ground water samples, respectively. Chloride concentration was in the range (167.04 to 370.01), (216.81 to 433.75) and (148.61 to 209.45) ppm in tap, river and ground water samples, respectively. Magnesium concentration was in the range (7.87 to 18.91) ppm, (18.53 to 33.33) ppm and (15.53 to 23.09) ppm in tap,river and ground water samples, respectively. Iron concentration was in the range (0.135 to 0.273) ppm, (0.127 to 0.221) ppm and (0.078 to 0.095) ppm in tap, river and ground water samples, respectively. Lead concentration was in the range (0.008 to 0.013) ppm in the tap water and its concentration was not found in both river and ground water.

Introduction

Water is one of the important commodities which man has exploited than any other resource for sustenance his life (1). Ground water comes from the small percentage of precipitation that falls, infiltrates the ground, traveling downward, and fills the available pore space within rock, sand gravel and clay. This forms a large subsurface storage area of water that interact with various rocks, minerals, and any man-made or natural material that may seep from the surface. Any substance that comes in contact with the ground water can affect water quality (2).

Water quality is of great importance because of an increased interest in health, coupled with information about our environment (3). It can be said that no water is pure or clean owing to the presence of some quantities of gases, minerals and living organisms. However, for practical purposes, pure water is considered to be that which has low dissolved and suspended solids and obnoxious gases as well as low in biological life. Such high quality water may be required only for drinking purposes, while for other uses like agriculture and industry, the quality of water can be quite flexible (1).

Water quality is affected by natural processes and human activities. It is often thought that the chemical composition is the only factor involved. However, other conditions, such as biological, physical and radiological factors should be considered when mentioning water quality (2). The unique properties of water which make it universal solvent got a much greater tendency to get polluted. Water can be regarded polluted when it changes in quality or composition either naturally or as a result of human activities (1).

Water pollutant can be defined as physical, chemical or biological factors causing aesthetic or detrimental effect on aquatic life or on those who consume water (1). Drinking water may be reasonably expected to contain at least very small amounts of some pollutants. That's because as the water draw from-lakes, rivers, streams, ponds, reservoirs, springs and wells travels over the surface of land or through the ground, it picks up naturally occurring minerals. It can also picks up substances resulting from presence of animals or from human activity (4). The presence of contaminants does not necessarily indicate that water possesses a health risk. The majorities of water pollutants are, however, in the form of chemicals which remain dissolved or suspended in water and give an environmental response which is often objectionable. Sometimes physical and biological factors act as pollutants (1). Some of elements that exist in water such as Copper, Lead, Iron, Calcium, Magnesium and Chloride. Trace amount of copper exist widely in river, tap, pond, well and under ground water. The potential sources of copper pollution are smelting and refining industries; copper wire manufacturing, iron and steel industries, metal cleaning operations, plating paths, rinses and manufacturing of printed circuit (5). Exposure to lead comes from a variety of sources. Lead is present in the air, food and in the water. Lead rarely occurs naturally in drinking water resources. The most common cause of lead in drinking water is corrosion, a reaction between the lead pipes or solder and the water. Lead exposure is considered a major environmental health threat to young children (6). Iron is one of the earth's most plentiful resources, making up at least five percent of the earth's crust (7). Aeration of iron containing layers in the soil can affect both ground and surface water (8). Iron is considered a secondary or "aesthetic" contaminant (7). Dissolution of iron can occur as a result of oxidation and decrease in pH (9). Calcium is the fifth most abundant natural element. It enters the fresh water system through the weathering of rocks, especially limestone, and from the soil through seepage, leaching and runoff (10). The concentration of calcium in water depends on the residence time of the water in calcium-rich geological formations (11).

Magnesium in drinking water has been calculated to constitute some 10% of the daily population intakes (12). Magnesium from water is absorbed faster to a higher degree than magnesium from food such as milk (13). Magnesium is quickly expelled from the bodies of healthy humans (14). Chloride is one of the major anions found in water and is generally combined with calcium, magnesium, sodium or potassium (15). Chloride in drinking-water originates from natural sources, sewage and industrial effluents, urban runoff containing de-icing salt and saline intrusion. The main source of human exposure to chloride is the addition of salt to food, and the intake from this source is usually greatly in excess of that from drinking-water. Excessive chloride concentrations increase rates of corrosion of metals in the distribution system, depending on the alkalinity of the water. This can lead to increased concentrations of metals in the supply. No health-based guideline value is proposed for chloride in drinking-water. Table (1) shows some elements that may present in water and their maximum contamination level to cause health problems for the world organizations and comparison with the Iraqi standard specifications of the chemical prosperities (inorganic compounds) for drinking water constructed from the central organization of the standardization and quality control (C.O.S.Q.C)(16; 17).

Table (1): The maximum contamination level of elements in drinking water.

Elements	EPA *	Canada* *	EEC** *	Japan*** *	WHO**** *	C.O.S.Q.C
Chloride (ppm)	250	250		200	250	250
Copper (ppm)	1	<1	2	1	1-2	1
Lead (ppm)	0.015	0.01	0.01	0.05	0.01	0.01
Iron (ppm)	0.3	<0.3	0.2	0.3	0.3	0.3
Calcium (ppm)						50
Magnesium (ppm)						50

* US environmental protection agency.
** These limits are establishes by health Canada.
*** European economic commodity for environmental legislation.
**** in Japan these limits are established for ministry of health.
***** World health organization guidelines.

Material and Methods

All chemicals and reagents used in this work were of analytical grad, supplied from Fluka, BDH and /or Aldrich companies.

The samples were collected from different water resources (tap, river and ground water), from different Iraqi locations (Sulaimaniyah, Mosul, Diyala, Baghdad, Karbala, Najaf and Diwaniyah).

The collected water samples were stored in a poly ethylene bottles which were cleaned with deionized water and dried. River water samples were collected from or near the middle of the river and the samples were taken under the river surface that mean the bottle was immersed under river surface.

For all tap water samples, the water was drawn from the tap for 1 min before collecting. All water samples were kept in a cold place in order to keep the water fresh as possible.

Preparations of standard solutions

All solutions were prepared in doubly distilled deionized water (resistivity ~ 18 MΩ).

1- Preparation of standard solutions for ISEs measurements:

Calcium:

Calcium stock solution (1000 ppm) was prepared by dissolving (0.2768 gm) of anhydrous $CaCl_2$ in 100 ml deionized water in a volumetric flask. The preparation of ISA which is 4M KCl, by dissolving (29.816 gm) of KCl with 100 ml deionized water.

Copper:

Cupric stock solution (1000 ppm) was prepared by dissolving (0.251 gm) of $CuSO_4.5H_2O$ with 100 ml deionized water in a volumetric flask. The ISA which is 5M $NaNO_3$ was prepared by dissolving (42.490 gm) of $NaNO_3$ with 100 ml deionized water.

Chloride:

Chloride stock solution (1000 ppm) was prepared by dissolving of (0.210 gm) of KCl with 100 ml deionized water in a volumetric flask. The ISA was the same as for the copper.

Calibration of the ISEs:

The electrode has been calibrated by measuring a series of known standard solutions, made by serial dilution of the 1000 ppm stock solutions for full calibration.

The ISA must be added to the standard and sample solutions as (2% V/V).

Potential measurements:

The calcium, copper and chloride ion selective electrodes were used as indicating electrodes and single, double junction electrodes were used as reference electrodes. The e.m.f. measurements were carried out at room temperature using the following cell:

Reference electrode \ test solution \ ISE:

A calibration curves was constructed for each ISE using several standard solutions ranged from (1–1000) ppm Ca^{++}, Cl^- and (0.1-1000) for Cu^{++}. The test solutions were constantly stirred with magnetic stirrer. Calibration curves were then constructed by plotting the potential versus the log of the concentration.

From the calibration curves all statistical facts including: slope; correlation factor, concentration range and detection limit which characterized the electrodes were determined.

Samples analysis:

The concentrations of Ca^{+2}, Cu^{+2} and Cl^- in the samples (tap, river and ground water) were measured by multiple standard addition methods.

In the multiple standard additions method (MSA) a 0.1 ml of 0.1 M of standard solution is added to 20 ml of water sample solution, the e.m.f was recorded. Before and after each addition of standard solution. The addition of (0.1ml of 0.1M) of standard is repeated six times. The concentration of samples is then calculated by plotting the electrode potential after each addition versus the volume added of standard solutions and extrapolating the volume of the standard added to the sample as x axis to the anti log E/S as y axis.

2- Preparation of standard solutions for AAS measurements:

Calcium:

Calcium stock solution (1000 ppm) was prepared by dissolving (0.24973 gm) of $CaCO_3$ in 2.5 ml of 1 M hydrochloric acid, diluted to 100 ml in a volumetric flask with deionized water.

Copper:

Copper stock solution (1000 ppm) was prepared by dissolving (0.1 gm) of copper metal in 5 ml of 5M nitric acid, and then diluted to 100 ml in a volumetric flask with deionized water.

Lead:

Lead stock solution (1000 ppm) was prepared by dissolving (0.1 gm) of lead metal in 5 ml of 2M nitric acid, dilute to 100 ml in a volumetric flask with deionized water.

Iron:

Iron stock solution (1000 ppm) was prepared by dissolving (0.1 gm) of iron metal in 2 ml of 5M hydrochloric acid, dilute to 100 ml in a volumetric flask with deionized water.

Magnesium:

Magnesium stock solution (1000 ppm) was prepared by dissolving (0.1 gm) of magnesium metal in 5 ml of 5M hydrochloric acid, dilute to 100 ml in a volumetric flask with deionized water.

Calibration curve for atomic absorption measurements:

Standard solutions for magnesium and calcium were prepared by subsequent dilution of stock solution (1000 ppm) of magnesium and calcium ions diluted to (100, 50, 10, 5 and 1 ppm).

The standard solutions for each lead and copper ions were prepared by subsequent dilution of stock solution (1000 ppm) of lead and copper and diluted to (10, 5, 1, 0.5, 0.1 and 0.01 ppm).

Iron standard solutions were prepared by subsequent dilution of stock solution (1000 ppm) of iron to (10, 5, 1, 0.5 and 0.1 ppm).

All above standard solutions was diluted to 100 ml in a volumetric flask with deionized water.

Determination of chloride:

The preparation of stock solution of chloride (1000 ppm) was done by dissolving (0.210 gm) of KCl in 100 ml volumetric flask with deionized water. Chloride ion standard solutions (500, 100, 10 and 1) ppm was prepared from stock solution.

The procedure of determination the concentration of the standards and water samples for chloride was performed by taking 5 ml of sample or standard in 100 ml beaker, add 2 drops of $KCrO_4$ indicator and then titrate with 0.05M of $AgNO_3$ to the end point, the color will change from yellow to slightly brown (18).

Results

1- Quantitative analysis using ion selective electrodes:

A linear calibration curve was obtained extended from (1-1000) ppm for Calcium and Chloride and extended from (0.1-1000) ppm as shown in the following figures:

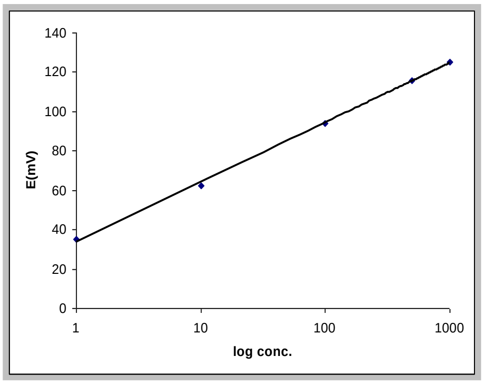

Figure (1): Calibration curve for calcium ion

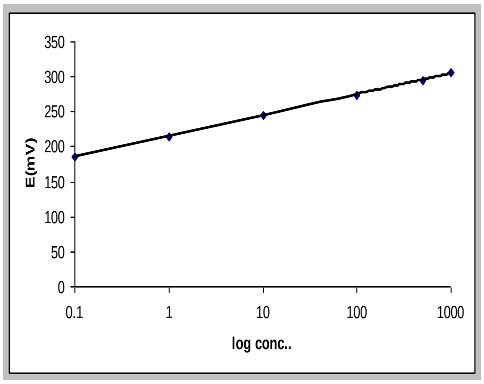

Figure (2): Calibration curve for cupric ion

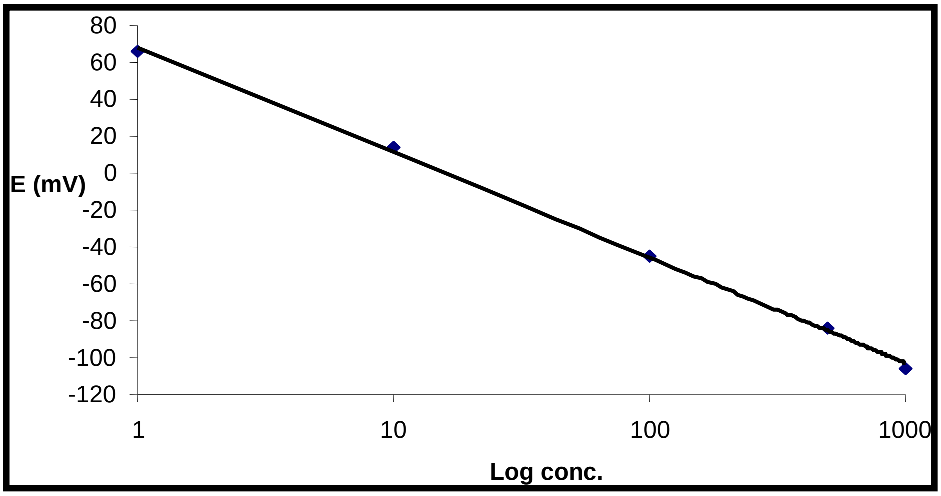

Figure (3): Calibration curve for chloride ion

Table (2): Shows the line equation and the correlation factor and the relative standard deviation and the slop for each electrode.

Ion	Line equation	Correlation factor	Slope	Relative standard deviation
Calcium	y = 30.259 Log x + 33.823	0.9995	30.259	0.0929%
Copper	y = 29.75 Log x + 214.99	0.9996	29.75	0.0282%
Chloride	y = -57.05 Log x + 68.246	0.9993	-57.05	0.136%

Table (3): Shows the recovery and error for the ions which determined by ion selective electrode.

Parameters	Ions		
	Calcium	Copper	Chloride
Concentration prepared (M)	1×10^{-3}	1×10^{-3}	1×10^{-3}
Found (M)	0.9813×10^{-3}	0.9715×10^{-3}	0.9931×10^{-3}
Recovery %	98.13	97.15	99.31
Error %	1.87	2.85	0.69

2- Quantitative analysis using atomic absorption spectroscopy:

A linear calibration curve was obtained extended from (0.1-10) ppm, for iron and (0.01-10) ppm for Lead and copper and (1-10) for magnesium and Calcium as showing in the following figures:

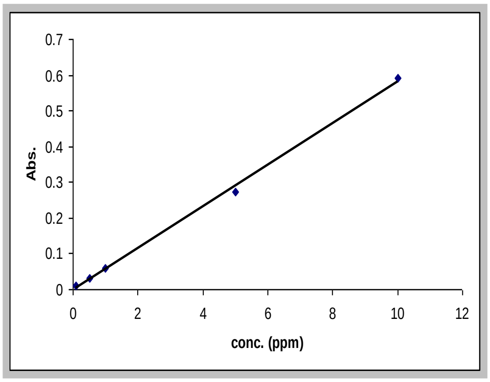

Figure (4): Calibration curve for Iron ion

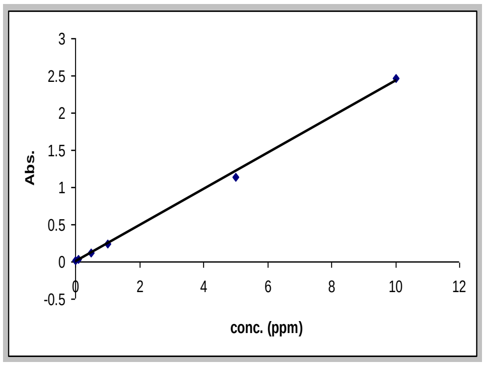

Figure (5): Calibration curve for leadion

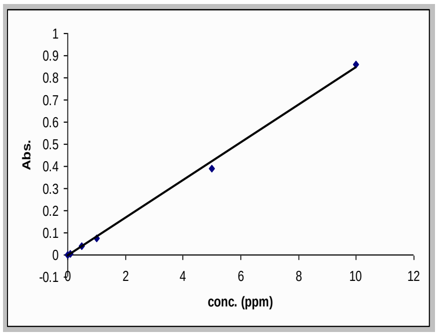

Figure (6): Calibration curve for Copper ion

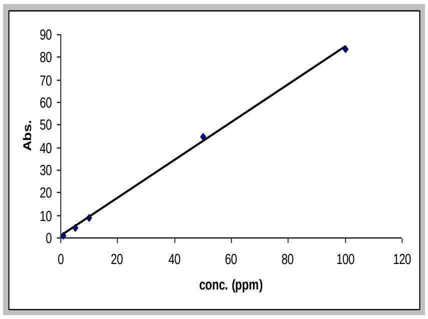

Figure (7): Calibration curve for

Table (4): Shows the line equation and the correlation factor and the relative standard deviation and the wave length for each ion measured by atomic absorption spectroscopy.

Ion	Line equation	Correlation factor	Wave length (nm)	Relative standard deviation
Calcium	$y = 0.6127x - 0.5464$	0.9993	422.5	3.57 %.
Copper	$y = 0.0853x - 0.0079$	0.9989	324.8	1.59 %
Iron	$y = 0.0584x - 0.0015$	0.9991	248.3	1.624%
Magnesium	$y = 0.8388x - 0.6867$	0.9993	285.2	0.0195 %
Lead	$y = 0.243x – 0.0068$	0.9992	283.8	3.144%

Table (5): Shows the recovery and error for the ions which determined by atomic absorption.

parameters	metals				
	copper	calcium	magnesium	lead	iron
Concentration prepared (M)	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}
Found (M)	0.9834×10^{-3}	0.9847×10^{-3}	0.995×10^{-3}	0.9798×10^{-3}	0.9867×10^{-3}
Recovery %	98.34	98.47	99.5	97.98	98.67
Relative Error %	1.66	1.53	0.5	2.02	1.33

Table (6): Shows the ion concentration in the ground water in some water resources.

location	Ion concentrations in river water (ppm)					
	Ca^{++}	**Mg**	**Cl^{-}**	**Cu^{++}**	**Fe**	**Pb**
Sulaimaniyah	32.42	15.53	148.61	0.035	0.095	____*
Baghdad (Qadissyah)	55.08	22.25	199.71	0.049	0.038	____*
Baghdad (Dora)	58.79	23.09	209.45	0.058	0.078	____*

* Not found

The highest concentrations of the metal ions in the ground water were found in Dora Baghdad, while the lowest concentrations were found in Al-Sulaimaniyah**,** except for the iron was higher in Al- Sulaimaniyah ground water samples than Baghdad ground water samples. Lead ion was not found in any sample while the highest concentration was for the chloride ion.

Table (7): Shows the concentrations of ions in the river water.

location	Ion concentrations in river water (ppm)					
Pb	**Fe**	**Cu**	**Cl**	**Mg**	**Ca**	
____*	0.127	0.036	216.81	18.53	39.19	**Mosul**
____*	0.139	0.044	280.45	20.54	43.21	**Diyala**
____*	0.145	0.045	255.18	24.56	50.81	**Baghdad**
____*	0.157	0.063	344.08	25.44	55.22	**Karbala**
____*	0.188	0.066	416.29	29.71	62.38	**Najaf**
____*	0.221	0.069	433.75	33.33	73.19	**Diwaniyah**

* Not found

Lead was not found in all these samples while chloride has the highest concentration. The metal ions concentrations were found to increase from the north down to the south of the both rivers (Tigris and Euphrates) this may be due to of the stripping of soil from the north to the south. Tigris river water has best water quality than Euphrates for approximately all metal ions which present in the river water, even for drinking water in the governorates which lies or near Tigris has a water quality better than the governorates which lies at Euphrates. This may be attributed to that Euphrates length about 2940 Km and pass through three countries (Turkey, Syria and Iraq), about 1160 Km of the river passed through Iraq. While Tigris length about 1800 Km and pass through Turkey and Iraq, about 1415 Km of the river passed through Iraq. Therefore, the industries and factories and other sources of water contamination may be the reason of its pollutants in the Euphrates than the sources of pollutants at Tigris.

Table (8) shown that the highest metal ions concentration in the tap water were found in Al- Diwaniyah while the lowest concentration were found in Al- Sulaimaniyah tap water samples.

Table (8): Shows the concentrations of ions in the tap water.

Ion concentrations in tap water (ppm)						**location**
Pb	**Fe**	**Cu**	**Cl**	**Mg**	**Ca**	
____*	0.135	0.053	167.04	7.87	20.73	**Sulaimaniyah**
____*	0.178	0.064	251.33	13.46	27.16	**Mosul**
0.0103	0.182	0.085	298.32	14.21	29.89	**Diyala**
0.008	0.191	0.071	246.37	9.53	23.16	**Baghdad (Qadissyah)**
0.011	0.198	0.072	399.59	12.23	26.45	**Baghdad (Dora)**
0.009	0.206	0.082	316.88	16.87	30.56	**Karbala**
0.012	0.211	0.096	327.61	17.65	39.89	**Najaf**
0.013	0.273	0.105	370.01	18.91	44.66	**Diwaniyah**

* Not found

Al- Najaf and Al- Diwaniyah have bad water quality compared with the other governorates for both tap and river water. For tap water the bad water quality may due to of their water treatment plant were not efficient to remove the high concentration of ions, for example in Al- Najaf according to some studies in their water treatment plant there has been no work on desalinization or other purification processes, which is critical and necessary in that areas (19). Also, in Al- Diwaniyah the network water pipes which supply the water from the water treatment plant was constructed from 1950'$_{s}$, this may be the main source of pipes corrosion (19). One other problem in the water treatment plant performance in these areas is the lake of electricity. Some of metals (copper, iron and lead), which determined in this study were found to be approximately higher in the tap water than river water. Corrosion which is caused when water reacted with or dissolves metal plumbing. This may added toxic levels of metals like copper and lead in tap water (19). The acidity and temperature of water can also increase the rate of pipes corrosion to a significant degree (20). The measured drinking water quality was in the range of acceptable values according to the Iraqi and international organization standards which were tabulated in the tables (1). However, there is some drinking water samples has contaminants concentration higher than the acceptable values. The calcium concentrations in drinking water in all samples were in the acceptable range which was (50 ppm). Magnesium in water samples was also in the acceptable range which was (50 ppm). Chloride in Al-Sulaimaniyah, Al- Mosul and Baghdad (Qadissyah Q.) was in the acceptable range which was (250 ppm), while the rest samples have chloride concentration higher than the acceptable range. For copper concentration in drinking water in all samples were in the acceptable value which was (1 ppm). However, in Al- Diwaniyah which has copper concentration in drinking water higher than the acceptable value according to Iraqi standard (C.O.S.Q.C), but in acceptable range according to EEC and Japan standards as shown in table (1). The iron concentrations in drinking water in all samples were in the acceptable value which was (0.3 ppm). Finally lead concentrations in Baghdad (Qadissyah Q.) and Karbala was in the acceptable range which was (0.01 ppm). The other drinking water samples the lead concentration was higher than the acceptable value according to Iraqi and some other standards. But, the US EPA and Japan water quality standards the maximum level is (0.015 and 0.05 ppm), respectively, according to these standards all samples will be in the acceptable range. The above values of some metal ions in water samples were measured using two methods. Calcium and copper were measured using both ion selective electrode and atomic absorption spectrometry, while chloride was measured using ion selective electrode and titration with silver nitrate. The results of the measurements were summarized and tabulated in table (9) for comparison.

Table (9): Metal ions concentration measured by ISE, AAS and the titration.

Chloride (ppm)		Copper (ppm)		Calcium (ppm)		location
Titration	ISE	AAS	ISE	AAS	ISE	
161.43	167.04	0.054	0.053	21.05	20.73	**Sulaimaniyah (TW*)**
153.77	148.61	0.039	0.035	32.91	32.42	**Sulaimaniyah (GW***)**
242.88	251.33	0.073	0.064	27.85	27.16	**Mosul (TW)**
210.34	216.81	0.042	0.036	39.18	37.39	**Mosul (RW)**
308.69	298.32	0.082	0.085	30.35	29.89	**Diyala (TW)**
271.02	280.45	0.047	0.044	43.87	43.21	**Diyala (RW)**
238.09	246.37	0.076	0.071	22.82	23.16	**Baghdad(TW) (Qadissyah Q.)**
192.99	199.71	0.053	0.049	56.58	55.08	**Baghdad(GW) (Qadissyah Q.)**
289.52	299.59	0.088	0.072	26.86	26.45	**Baghdad(TW) (Dora Q.)**
207.41	209.45	0.061	0.058	59.69	58.79	**Baghdad(GW) (Dora Q.)**
219.25	225.18	0.051	0.045	55.96	50.81	**Baghdad(RW)**
305.14	316.88	0.091	0.082	30.69	30.56	**Karbala (TW)**
356.04	344.08	0.065	0.063	56.07	55.22	**Karbala (RW)**
316.25	327.61	0.098	0.096	39.28	39.89	**Najaf (TW)**
402.44	416.29	0.069	0.066	63.51	62.38	**Najaf(RW**)**
357.57	370.01	0.12	0.105	45.23	44.66	**Diwaniyah (TW)**
419.17	433.75	0.071	0.069	73.37	73.19	**Diwaniyah (RW)**

* TW: Tap Water, **RW: River Water, ***GW: Ground Water

Discussion

This study included the determination of metal ions (calcium, copper, chloride, magnesium, iron and lead) in different water resources (tap, river and ground water samples), that were collected from some Iraqi governorates. River water of both Tigris and Euphrates rivers measured in this study were found to have the highest concentration level for all metal ions, in Al-Diwaniyah. While the lowest concentrations were found in Al- Mosul. Most of metal ions concentrations were found to increase from north down to the south of the rivers for both Tigris and Euphrates rivers. Water quality in Tigris river was better than the water quality in Euphrates river. Lead was not found in the river water of all samples.

The lowest concentrations of the metal ions in the ground water were found in Al-Sulaimaniyah and the highest were found in Dora Baghdad, for all metal ions except the iron which was the highest in Al-Sulaimaniyah, while the lowest iron concentration was found in Baghdad ground water samples. Lead also was not found in the ground water samples.

For tap water the highest concentration of (calcium, magnesium, copper, chloride, iron and lead) were found in Al- Diwaniyah, while the lowest were found in Al-Sulaimaniyah. Most of the drinking water samples were in the acceptable range according to Iraqi and the international water quality specifications.

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تقدير تركيز بعض الأيونات المعدنية في بعض مصادر المياه العراقية

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كلية العلوم – جامعة النهرين

الخلاصة

في هذا البحث تم دراسة نوعية المياه في بعض مصادر المياه العراقية، اذ جرى تقدير تراكيز بعض الايونات والمعادن في بعض مصادر المياه كماء الشرب وماء النهر وماء البئر، وتضمنت النتائج تعيين تراكيز ايونات الكاليسيوم والمغنيسيوم والكلورايد والنحاس وعنصري الحديد والرصاص في بعض مصادر المياه العراقيه المذكوره سابقا، وتراوح تركيز الكالسيوم بين 20.73–44.66 ملغم/لتر، 39.19–73.19 ملغم/لتر، و32.42–58.79 ملغم/لتر في ماء الشرب والنهر وعينات ماء البئر على التوالي، وتراوح تركيز النحاس بين 0.053–0.105 و0.036–0.069 و0.035–0.058 ملغم/لترفي ماء الشرب والنهر وعينات ماء البئر على التوالي، وتراوح تركيز الكلورايد بين 167.04–370.01 و216.81–433.75 و148.61–209.45 ملغم/لتر في ماء الشرب والنهر وعينات ماء البئر على التوالي، وتراوح تركيز المغنيسيوم في عينات المياه بين 7.87–18.91 ملغم/لتر و18.53–33.33 ملغم/لتر و15.53–23.09 ملغم/لتر في ماء الشرب والنهر وعينات ماء البئر على التوالي، وتراوح تركيز الحديد في عينات المياه بين 0.135–0.273 ملغم/لتر و0.127–0.221 ملغم/لتر و0.078–0.095 ملغم/لتر في ماء الشرب والنهر وعينات ماء البئر على التوالي، اما تركيز الرصاص في عينات مياه الشرب فكان يتراوح بين 0.008–0.013 ملغم/لتر ولم يوجد تركيز للرصاص لا في عينات مياه النهر ولا في عينات مياه البئر في هذه الدراسة.