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Hydrogeochemistry Study of Groundwater and Identify their Origin in the Region Surrounding of Ramadie City in Al - Anbar Province, Iraq

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Abstract
Hydrogeochemical study and identify the origin of water wells were curried out in the region surrounding of Ramadie city in Al-Anbar province, Iraq. Results of the study showed that the groundwater in the study area mostly is very hard and alkaline nature as hardness values ranged 324.2 to 1763.5 and as pH values ranged 7.12 to 7.81 respectively. It has conducted a test of accuracy of the chemical analysis for collected water samples and shows it's very accurate and within the permissible limits and reliable in the chemical interpretation. In the present study "Piper diagram" have been used for manipulating analytical data to estimate the chemical type of groundwater in the study area. Depending on this diagram the groundwater in the study area is considerably dominated by Sulfate type and four hydrochemical facies of water have been detected. These facies are "Na^{+}- SO_4^{2-} ", "Na^{+}- Cl^{-} "," Mg^{2+}- SO_4^{2-} " and " Ca^{2+}- SO_4^{2-} ". To decide the groundwater origin of hydrochemical functions such as rCa / rCl rMg / rCl, rNa / rCl, rK / rCl, and rSO_4 / rCl in the studied water samples have been calculated and compared with the standard values of the seas and oceans waters. The result shows that the origin of the water in the study area is infiltrated meteoric.

Key words: Hydrochemistry, Groundwater Origin, Piper Diagram, Hydrochemical Functions

Introduction
The hydrochemistry of groundwater study is one of the important studies in order to obtain new water sources as possible to be used for the development of irrigation, agricultural, industrial areas and for the drinking purposes [13] and [23]. These sources can be use after modern purification processes by an operation to get rid salt and germs by using the process of chemical and biological analysis. It may be noted that many countries especially neighboring countries consider the groundwater are the main source of water so as to lack of rivers and other source of water. General Company for drilling wells has been drilled a number of wells around the Ramadi city. Seventeen wells were selected for the purpose of the current study which is located around the Ramadi city between latitudes 32° 55' 00" to 33° 26' 05" North and longitude 42° 31' 11" to 43° 47' 21" East (Fig. 1). The main objective of the current search is to study the hydrochemistry and identify the origin of groundwater in the region surrounding of Ramadie City. A large number of studies have addressed this subject in recent years, including [4], [1], [2] and [10]

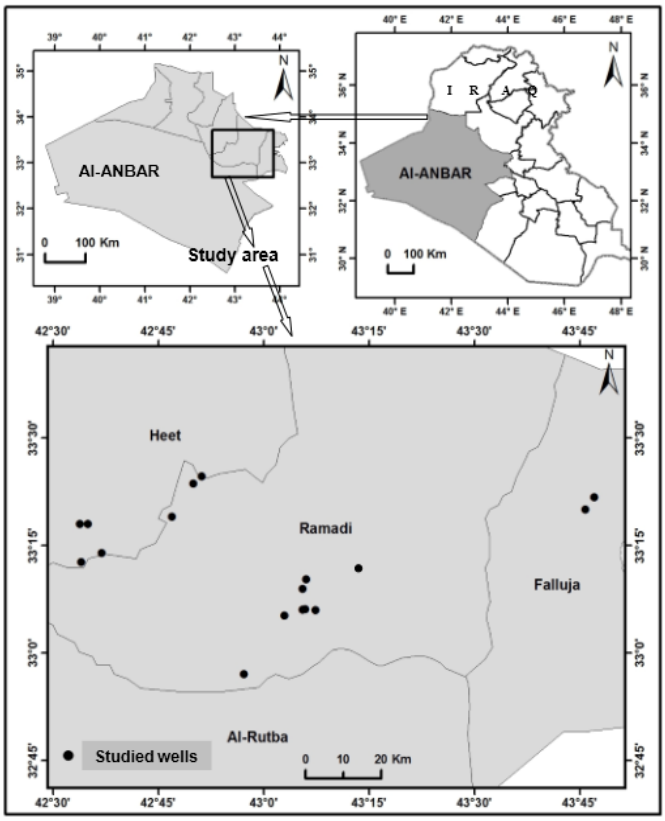

Figure (1): Location map of the study area showing studied water wells

Geological Description of the Study Area

Injana and Fatha Formation represents the main formation in the study area and covered by alluvium sediments which consist mainly of fine to medium gravel and colored sand overlapping with silt and clay sediments [24] and [20]. Secondary gypsum deposits were presented in alluvium deposits resulting from the formation of Bakhtiari [8]. The study area characterized by the absence of folds and faults and this confirms that there are no tectonic movements in the region. Due to the low permeability of the layers or deposits, lack of rainfall and high evaporation rates, the possibility appearance of groundwater is poor and quality of ground water is unsuitable for human use so it is used exclusively for specific purposes only, due to the high concentration of total dissolve solid (TDS) in the groundwater [16].

Climate

Recorded of the temperatures within the study area is -7.6^{o} C to 50.7^{o}C and annual radiation of the sun's energy ranges between (240-750) mille watts / cm^{2} in every 8.8 hours of radiation on day [5]. Rainfall in Al-Anbar province in which the study area is located is intermittent and highly variable in space and varying between 50-150 mm/year [5]. The average monthly of evaporation in the study area ranged between (150 - 183) mm and annual rates between (1260 - 2200) [5]. Relative humidity values in the study area ranged from 22 to 76 %, where the annual average relative humidity less than 50%. All climate information's were recorded in Ramadi stations for the period of 1967 to 2010 [9]. According to the climatologically factors which have discuses above, the study area is mainly affected by dry desert climate.

Methodology

Seventeen wells drilled in the study area by the General Directorate of drill water wells in Baghdad have been selected. Global Position System (GPS) system has been used to determine the wells locations and heights above sea level as shown in (Fig.1) and Table (2) respectively. Seventeen water wells sample collected from different site of the search area have been subjected to physiochemical analysis in the Directorate-General for the drilling of wells laboratory. The water wells sample were analyzed by standard methods for water analysis [13] which are listed in Table (1) and the measured values of physiochemical analysis are presented in Table (2).

Table (1): A summary of the methods used for the analysis of water samples

Serial No	Parameters	Methods
1	pH, Total Dissolve Solid (TDS) and Electrical Conductivity (EC)	Electrolytic
2	Na^{2+} and K^{+}	Flame photometer
3	Ca^{2+}, Mg^{2+},	EDTA titration
4	HCO^{3-},	H_2SO_4 titration
5	Cl^{-}	$AgNO_3$ titration
4	SO_4^{2-}	Spectrophotometers

Table (2): Chemical analysis of collected well water samples (Units in ppm except Electrical conductivity (EC) in µs.cm^{-1})

Well No.	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{2-}	Cl^{-}	Depth (m)	Eleveation (AMSL)
W1	7.12	3230	2330	210	87	318	8	260	624	497	140	94
W2	7.43	8470	4000	402	185	294	20.5	85	1358	656	100	91
W3	7.14	4690	3312	285	130	460	23	410	912	696	100	92
W4	7.2	2690	1862	175	60	248	3	220	560	340	100	87
W5	7.2	3400	2426	235	102	350	12	285	720	554	100	93.5
W6	7.19	3990	2922	211	110	359	5	245	866	455	130	91
W7	7.41	3880	2858	269	170	248	6	260	1026	441	120	93.5
W8	7.27	4200	3038	300	140	446	20.8	261	1180	614	200	92.5
W9	7.22	3550	2310	181	88.1	410	5.35	365	655	497	142	91
W10	7.22	2970	2136	69	37	428	14	268	512	361	90	89.6
W11	7.41	3230	2465	187	88	322	4.6	441	683	331	108	89
W12	7.81	3630	2474	171	128	423	7.1	290	789	553	99	102
W13	7.22	1610	1100	89	68	79	5	48	361	170	90	93
W14	7.21	3150	2300	160	96	190	4	101	798	171	112	91
W15	7.16	3770	2712	200	160	262	14	212	845	490	150	95
W16	7.81	3630	2723	171	125	423	7.1	290	759	583	130	91
W17	7.2	815	625	84	29	49	11	64	254	75	201	110

Accuracy of Analysis

Many errors can occur in analysis while conducting tests, including chemical reagents used for the analysis or human error or distilled water quality etc. [7]. Therefore it is necessary to be determined the accuracy of the analysis. In the present study the accuracy of analysis which is called a relative difference (R.D) has been calculated using the flowing relationship [15].

$$R.D = (\sum Cation - \sum Anion) / (\sum Cation + \sum Anion)*100 \quad \ldots\ldots 1$$

Which represents the ratio between the different summation of cation concentrations and the concentrations of Anion ions divided by the total summation in units of equivalent per million (epm), multiplied by 100. If the value of R.D is less than 5% the accuracy of the analysis is very high and if between 5% -10% are medium and if it is greater than 10% is not possible rely on the analysis of changes in the hydrochemical [7]. When using the accuracy of analysis (R.D) method in the present study as shown in Table (3), it has observed that chemical analysis of water samples were accurate and within the permissible and reliable in the chemical interpretation.

Table (3): Relative difference of chemical analysis in the present study

Well No.	∑Cation	∑Anion	R.D	Type
1	31.66	31.26	0.63	Certain
2	48.57	48.16	0.42	=
3	45.49	45.33	0.18	=
4	24.53	24.85	0.65	=
5	35.63	35.28	0.50	=
6	35.30	34.87	0.61	=
7	38.32	38.06	0.34	=
8	46.40	46.16	0.26	=
9	34.23	33.63	0.89	=
10	25.45	25.23	0.43	=
11	30.68	30.78	0.17	=
12	37.61	36.77	1.14	=
13	13.59	13.10	1.84	=
14	24.23	23.10	2.40	=
15	34.86	34.88	0.03	=
16	37.37	36.99	0.51	=
17	8.99	8.45	3.07	=

Calculation of Total Hardens

Total Hardness (TH) is a measure of the amount of calcium and magnesium ions present in the water expressed as equivalent mass of calcium carbonate per volume of water which can be calculated using the fallowing relationship [22].

$$TH = 2.5(Ca^{2+}) + 4.1(Mg^{2+}) \quad \ldots 2$$

Where the concentration of Ca^{2+} and Mg^{2+} are expresses in parts per million (ppm) units. The total hardness values were calculated for the water sample collecting from the studied wells and it is ranging from 324.2 to 1763.5 as shown in Table (4). With correlated these values with the values that have been identified by [22] as shown in Table (4), it has been observed that the groundwater in the study area mostly is very hard. In addition to determining the water hardness the nature of water well in the study area also has been determined through pH values which ranging from 7.12 to 7.81 and this indicates that the water in the study area is alkaline nature.

Results and Discussion

Hydrochemical classification

There are several methods used for hydrochemical classification including Schoeller [19], Sulin [21], and Piper [18], and all these methods designed to identify water quality, source, origin and the balance between the different water sources. The best graphical method is the Piper diagram due to it can be plotted a lot of water analysis on the same diagram as well as it can be used to classify water and to identify the mixing of type's water. In the present study reacting values of major ions have been plotted in "Pipers trilinear diagrams" as shown in (Fig. 2). It has been observed

Table (4): Hardness values for the water sample collecting and water hardness classification accords [22].

Hardness values for the water sample				Water hardens [22]	
Well No.	Ca^{+2} (ppm)	Mg^{+2} (ppm)	Total Hardens (TH)	Water class	Hardens (ppm)
W1	210	87	881.7	Soft	0 -75
W2	402	185	1763.5	Moderately	75-150
W3	285	130	1245.5	Hard	150-300
W4	175	60	683.5	Very Hard	>300
W5	235	102	1005.7		
W6	211	110	978.5		
W7	269	170	1369.5		
W8	300	140	1324.0		
W9	181	88.1	813.7		
W10	69	37	324.2		
W11	187	88	828.3		
W12	171	128	952.3		
W13	89	68	501.3		
W14	160	96	793.6		
W15	200	160	1156.0		
W16	171	125	940.0		
W17	84	29	328.9		

that the among major cations of the well water samples are mostly located close to the (Mg^{2+} + Na^{2+}) end while in the triangle of anions the position of the water wells indicates dominance of SO_4^{2-} with significant portion of Cl^- but comparatively low HCO_3^{1-} in the water", Hence, water wells in the study area is considerably dominated by Sulfate type and four hydro-chemical facies can be chemically distinguished such as: " Na^+- SO_4^{2-} facies", " Na^+- Cl^- facies", "Mg^{2+}- SO_4^{2-} facies", and " Ca^{2+}- SO_4^{2-} facies". The first hydro-chemical facies (Na^{+2}-SO_4^{2-}) is a bulk which is the predominant facies in the study area and represent 41.2% as shown in Table (5). Type II (Na^{2+}- Cl^-) accounts about 30% of the studied water samples. Type III accounts for about 17.6 % of the total samples studied and the fourth type accounts for 11% of the total number of samples studied.

Table (5): Types of water in the studied wells

Well No	Type of water	Percentage of studied water sample
1, 3, 5, 9,16	Na-Cl	29.4%
2, 17	Ca-SO_4	11.8%
4, 6, 8, 10, 11, 12, 14	Na-SO_4	41.2%
7, 13, 15	Mg-SO_4	17.6%

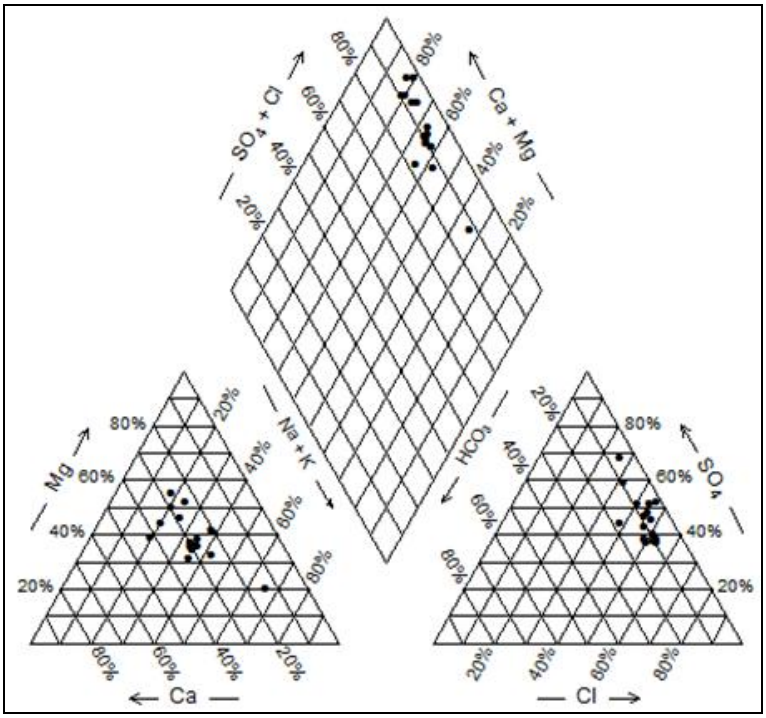

Figure (2): Pieper diagram showing the chemical composition of groundwater in the study area

Origin of Groundwater in the Study Area

The study of hydrochemical functions for water is one of the important topic in determining the origin of water in addition to the studying of changes that obtain on major ions, especially when compare these values with sea water where that the ratio of major ions to chloride for seawater is fixed for all solutions which reach to saturation for salt of halite [11]. According to [17] the water within the earth's crust is divided on the basis of their origin to the meteoric water or sea water. To decide the groundwater origin in the study area four hydrochemical coefficients have been used such as rCa / rCl rMg / rCl, rNa / rCl, rK / rCl, and rSO_4 / rCl [12] . These are the main hydrochemical functions which are taken the respectively values 0.4, 0.2, 0.85, 0.2 and 0.1 of seas and oceans water as a standard values which used to determine the origin of the water in the study area. The small letter (r) in all functions indicates that the units used in the calculation of these functions are equivalent per million (epm). It has been chosen the chloride ion to know the geochemical behavior of each element by the ratio of each element to the chloride ion and this is term "hydrochemical function". This is because of the chloride ion is more elements scalability solubility and less ions affected by the physical and chemical variables in the water in addition to that it is not affected by operations of adsorption and ion exchange by clay minerals [14]. The hydrochemical functions of the water wells sample have been calculated and compared with the standard values of the seas and oceans waters. The calculated values have been presented in Table (6).

rCa/rCl

The calculated rCa/rCl values of the studied water well were exceeding standard sea water in all samples except well number 10 because of the increasing of

Table (6): Calculated values of hydrogeochemical functions in the studied wells

Well No.	"Hydrochemical functions "				
	"rCa /rCl"	"rMg/Cl"	"rNa/rCl"	"rK/rCl"	"rSo_4/ rCl"
1	0.75	0.51	0.99	0.01	0.93
2	1.09	0.82	0.69	0.03	1.53
3	0.73	0.54	1.02	0.03	0.97
4	0.91	0.51	1.13	0.01	1.22
5	0.75	0.54	0.98	0.02	0.96
6	0.82	0.70	1.22	0.01	1.41
7	1.08	1.12	0.87	0.01	1.72
8	0.87	0.66	1.12	0.03	1.42
9	0.65	0.52	1.27	0.01	0.97
10	0.34	0.30	1.83	0.04	1.05
11	1.00	0.77	1.50	0.01	1.53
12	0.55	0.67	1.18	0.01	1.06
13	0.93	1.16	0.72	0.03	1.57
14	1.66	1.63	1.71	0.02	3.45
15	0.72	0.95	0.83	0.03	1.28
16	0.52	0.62	1.12	0.01	0.96
17	1.99	1.13	1.01	0.13	2.50

the Ca^{2+} ion concentration in the water (Fig. 3). There are two major process explain increasing of ion concentration of calcium in the water. The first process is the cation exchange between Mg^{2+} in the water with Ca^{2+} in the surrounding rocks during the hydrochemical formation of the old marine water genesis. The second process is from the discharge process of the aquifer materials as a result of deep meteoric water percolation [12].

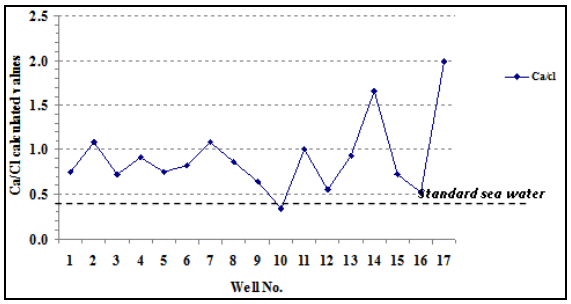

Figure (3): Values of rCa / rCl for all studied wells water

rMg /rCl Function

It has been observed from the (Fig. 4) that the hydrochemical parameters of rMg /rCl more than the standard value of sea water in all samples. The observed high value of Mg^{2+} ion concentration in all studied sample is because of the exceedingly flushing action of the percolating meteoric water and the process of leaching of meteoric water on constituents of rock [12].

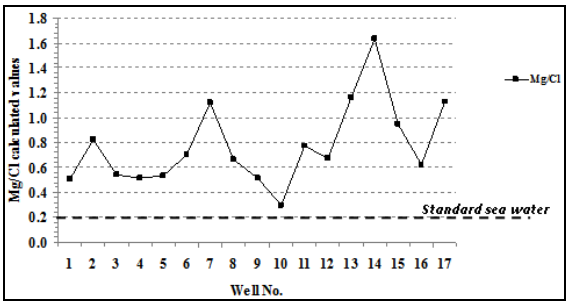

Figure (4): Values of rMg / rCl for all studied wells water

rNa/rCl Function

It is one of the best functions in determining the origin of groundwater where it will be more than one in the meteoric and it will be less than one in the marine water [12]. (Fig.5) shows the value of the function of the water samples in the study area which is ranging from 0.69 to 1.83 and an average of 1.13. In correlated these values with the standard sea water it is observed that the rate is much higher than one thus, these waters are meteoric origin.

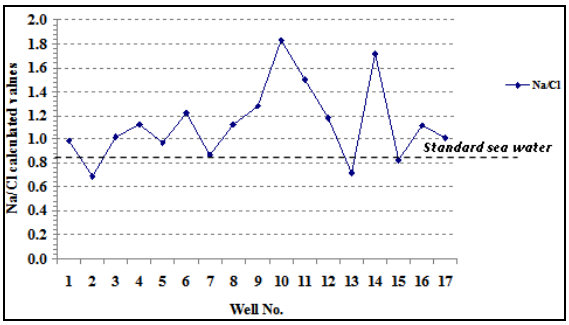

Figure (5): Values of rNa / rCl for all studied wells water

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rK/rCl Function

The rK/rCl values ranging from 0.13 to 0.01 in the studied well water as shown in (Fig.6) and it is found to be less than standard sea water value including all water samples. The decreasing $\mathbf{K^+}$ ionic concentration in the water samples below seawater may indicate that depletion of $\mathbf{K^+}$ in the well water sample either due to the low amount of potassium in the sediments or adsorbed the $\mathbf{K^+}$ by clay minerals such as montmorillonite and illite [3].

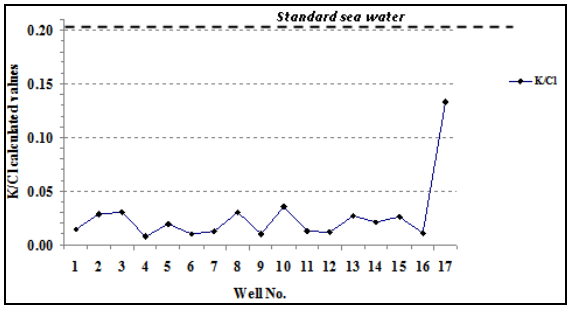

Figure (6): Values of rK / rCl for all studied wells water

rSO_4/ rCl Function

It is playing a prominent role in ground water study because it is very common ions in the study area. In all studied wells the rSO_4 / rCl were observed more than the standard seawater value (Fig.7). The increase of sulfate ion concentration is mainly because of dissolve the gypsum occurred in the soil of the study area or due to the leaching process of meteoric water percolation [3].

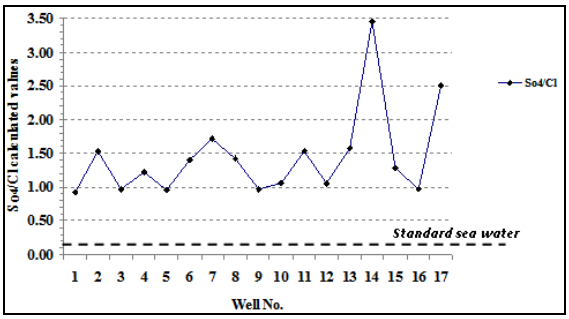

Figure (7): Values of rSO_4 / rCl for all studied wells water

Conclusion

The main objective of the current study is to evaluate the chemistry of water wells and determine their origin in the region surrounding of Ramadie City in Al-Anbar province, Iraq. Interpretation of hydrochemical analysis reveals that the groundwater in area is very hard and mostly alkaline in nature. Based on "Piper diagram", show that the water wells in the study area is considerably dominated by Sulfate type, and four facies of groundwater were chemically distinguished: " Na^+- SO_4^{2-} facies ", " Na^+- Cl^- facies", " Mg^{2+}- SO_4^{2-} facies" ,and " Ca^{2-}- SO_4^{2-}facies " The Na^+- So_4^{2-} facies represent the large portion while the Ca^{2+}- SO_4^{2-} facies represent the latest. The origin of water wells have been identified using four hydrogeochemicl funcution such as rCa / rCl, rMg / rCl, rNa / rCl, rK / rCl, and rSO_4 / rCl in the study area. These functions have been calculated and compared with the standard values of the seas and oceans waters. The result shows that the origin of the water in the study area is infiltrated meteoric.

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دراسة هيدروجيوكيميائية المياه الجوفية و تحديد مصدرها في المناطق المحيطة بمدينة الرمادي في محافظة الأنبار / العراق

مفيد الحديثي

المعهد التقني الانبار ، الجامعة التقنية الوسطى ، الانبار ، العراق

الملخص

تم في هذا البحث اجراء دراسة هيدروجيوكيميائية المياه الجوفية وتحديد اصلها للأبار في المناطق المحيطة بمدينة الرمادي في محافظة الانبار/ العراق. أظهرت نتائج الدراسة أن المياه الجوفية في منطقة الدراسة هي عسرة جدا وذات طبيعة قاعدية حيث تراوحت قيم العسرة من 324.2 الى 1763.5 وقيم درجة الحموضة تراوحت من 7.12 الى 7.81 على التوالي وقد تم اجراء اختبارا لمدى دقة التحليل الكيميائي لعينات المياه التي تم جمعها وتبين انها دقيقة جدا وضمن الحدود المسموح بها ويمكن الاعتماد عليها في التفسير الكيميائي. في الدراسة الحالية تم استخدام مخطط بايبر في معالجة البيانات المحللة لغرض تحديد نوعية مياه الابار في منطقة الدراسة واعتمادا على هذا المخطط تبين ان نوعية المياه السائدة في منطقة الدراسة هي نوع الكبريتات وقد اشر تواجد اربع انواع من السحنات الهيروكيميائية لمياه الابارالمدروسة وهي: "Na^{+}- SO_4^{2-} ", " Na^{+}- Cl^{-} ", " Mg^{2+}- SO_4^{2-} ", "Ca^{2-}- SO_4^{2-} " . ولغرض تحديد اصل المياه في منطقة الدراسة تم استخدام الدوال الهيدروكيميائية مثل "rCa / rCl, rMg / rCl, rNa / rCl, rK / rCl, rSO_4 / rCl وقد قورنت مع القيم القياسية للبحار والمحيطات وبينت النتائج ان نوع المياه في منطقة الدراسة هي ذات اصل جوي مترشح.

الكلمات الدالة: كيميائية المياه , اصل المياه الجوفية , مخطط بايبر, الدوال الهيدروكيميائية