

1. Introduction

1.1 Water resources

Water is one of the important commodities which man has exploited than any other resource for sustenance his life. Most of the water on this planet is stored in oceans and ice caps which is difficult to be recovered for our diverse needs. Most of our demand for water is fulfilled by rain water which gets deposited in surface and ground water resources ^[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].

1.1.1 Water quality

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

determination of inorganic constituents and their impact on water quality require an in-depth knowledge of the interactive water chemistry relationship ^[4]. 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. Thus, becoming less suitable for drinking, domestic, agriculture, industrial, recreational, wildlife and other uses for which it would have been otherwise suitable in its natural or unmodified state ^[1].

1.1.2 Water pollutants

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 ^[5]. 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].

1.1.2.1 Some of elements that exist in water

- **Copper**

Trace amount of copper exist widely in river, tap, pond, well and under ground water. This metal is essential trace element for biological system. Numerous dissolving chemical forms, such as aqua ions, complexes and colloids, are observed in natural water. In general the toxicity of dissolved copper (Cu^{++}) is considered to be much less than that of mercury, but greater than that of cadmium, silver, lead and zinc ^[6].

Copper is widely used in the production of wire, brass; boiler pipe, cooking utensils, and fertilizers, etc. Copper sulfate has been used in reservoirs and distribution system as an algicide ^[7]. Therefore, copper is frequently found in water and waste water at significant quantities.

Although copper is known to be a biologically essential and beneficial element, ingestion of excessive copper can cause nausea, vomiting, diarrhea, epigastric pain, and dizziness.

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 ^[7].

- **Lead**

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. Drinking water contributes an estimated 15 to 20 % of the exposure to lead in humans. In addition lead ingested from water is absorbed more completely than lead from food. In adults, 10 to 15 % of lead in food is absorbed but 35 to 50 % or more of lead in water is

absorbed ^[8]. The most common source of lead in water are lead service line that connect water mains to homes, lead solder and pipes within homes, and brass plumbing fixtures. 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 ^[9]. It reduces birth weight, causes premature birth, delays physical and mental development in babies and young children, and impairs mental abilities in children in general. In adults, lead can increase blood pressure and interfere with hearing. At high level of exposure, lead can cause anemia, kidney damage and nerve damage. However, young children and pregnant women are the most risk ^[8].

- **Iron**

Iron is one of the earth's most plentiful resources, making up at least five percent of the earth's crust ^[10]. Aeration of iron containing layers in the soil can affect both ground and surface water ^[11].

Iron is considered a secondary or "aesthetic" contaminant ^[10]. Dissolution of iron can occur as a result of oxidation and decrease in pH ^[12]. In fact, iron is essential for good health because it transports oxygen in blood ^[10]. Iron in water is not a health hazard by itself since many organisms require iron to grow ^[13].

- **Calcium**

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 ^[14]. The concentration of calcium in water depends on the residence time of the water in

calcium-rich geological formations ^[15]. Calcium blocks the absorption of heavy metals, and it has been found, for example, that low calcium diet increases the susceptibility of rates of lead poisoning ^[16]. Calcium is necessary for good health ^[17]. Drinking water containing calcium may provide a significant portion of the required daily intake to prevent such as osteoporosis, hypertension and cardiovascular disorder ^[18].

- **Magnesium**

Magnesium in drinking water has been calculated to constitute some 10 % of the daily population intakes ^[19]. Magnesium from water is absorbed faster to a higher degree than magnesium from food such as milk ^[17]. Magnesium is quickly expelled from the bodies of healthy humans ^[20]. Excess of magnesium may cause kidney diseases, however, may suffer from hypertension, confusion, muscle weakness and coma ^[19].

- **Chloride**

Chloride (Cl⁻) is one of the major anions found in water and is generally combined with calcium, magnesium, sodium or potassium ^[21].

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. However,

chloride concentrations in excess of about 250 mg/liter can give rise to detectable taste in water ^[22].

Table (1-1) shows some elements that may present in water and their maximum contamination level to cause health problems for the world organizations ^[23].

Table (1-1) the maximum contamination level of elements in drinking water

elements	EPA*	Canada**	EEC***	Japan****	WHO*****
Chloride (ppm)	250	250		200	250
Copper (ppm)	1	<1	2	1	1-2
Lead (ppm)	0.015	0.01	0.01	0.05	0.01
Iron (ppm)	0.3	<0.3	0.2	0.3	0.3

*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

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) is shown in table (1-2)

Table (1-2) the maximum level of elements in drinking water according to (C.O.S.Q.C) [24]

elements	Maximum level
Lead (ppm)	0.01
Copper (ppm)	1
Iron (ppm)	0.3
Calcium (ppm)	50
Magnesium (ppm)	50
Chloride (ppm)	250

1.1.3 Origin and source of water pollution

1.1.3.1 Origin and sources of water pollutants

The origin of pollutants can be traced to their natural occurrence on the earth, formation by transformation and concentration of natural substances, and their man-made synthesis. The pollutant may arise quite naturally to form part of the background concentrations in the environment. The example of some naturally occurring pollutants forming the background is oxides of nitrogen, heavy metals and hydrocarbons. Some pollutants can be formed by concentration and transformation of naturally occurring compounds during their domestic, agriculture or industrial use. The generation of sewage and waste waters containing agrochemicals, certain pesticides and surfactants, petrochemicals, hydrocarbons and heavy metals are some important examples of pollutants originated in this way. Many chemicals do not occur

in the nature, and pollution caused by them is entirely man-made, for example, synthesis of various pesticides, surfactants, plastics and petrochemicals has introduced a large number of chemicals in environment which created severe environmental problems. Many of them move from one component to another (*air = water, air = soil, soil = water*), finally, contaminate the whole environment ^[1].

1.1.3.1. a- Natural source of *run-off* ^[1]

The natural entry of pollutants in water bodies can take place through rain; from atmosphere by dry deposition entrainment and reaction; periodic submergence of surrounding vegetations, and falling of dry parts of nearby vegetation directly on the surface of waters. The *run-off* water originated from different areas is quite rich in nutrients and organic matter. The *run-off* from sparsely populated or rural areas can pick up several substances from soil, including nutrients and organic debris.

The *run-off* water originates from the urban areas can collect vast quantities of substances from roadside waste waters drains, surface of roads, open areas and from houses.

1.1.3.1. b- Domestic sewage ^[1]

Sewage consists of waterborne wastes of community, and contains about **99%** of water and **1%** of solids. Of solids present in sewage, **70%** are organic and **30%** are inorganic in nature. Out of the organic constituents, **65%** are proteins, **25%** are carbohydrate and **10%** fats, as shown in figure (1-1).

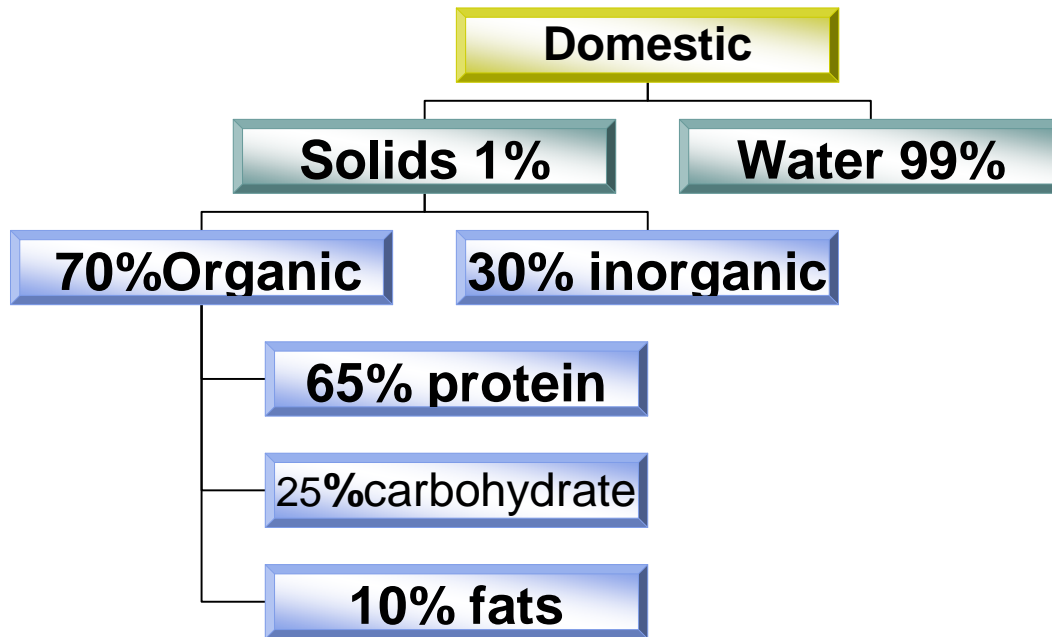


Figure (1-1) the distribution of domestic sewage components.

The inorganic fraction of sewage constituents are grit salts and metals in varying proportions. In most cases the domestic sewage is generally discharged as untreated or partially treated form to the nearby water bodies like rivers, lakes, estuaries or coastal water where it can cause severe sanitary and other water pollution problems.

1.1.3.1. c- Agriculture wastes ^[1]

Agriculture wastes usually originate in the form of *run-off* from the agricultural fields and animals farms. Modern agriculture uses a large number of chemicals, called agrochemicals, in the form of fertilizers, organic manures, pesticides, growth hormones, nutrient solutions and others. All the residual forms of these chemicals along with organic debris from the remains of the harvested crops are trapped by *run-off* water causing pollution problems in the receiving waters. The agricultural *run-off* is considerably rich in nutrient like nitrogen and phosphorus. While nutrients

create problem of eutrophication, pesticides are responsible for causing toxicities to aquatic life. Several pesticides have been reported to get bioaccumulated and biomagnified through food chains resulting in the secondary poisoning to man and predatory birds.

1.1.3.1. d- Industrial wastes ^[1]

Industrial wastes have the greatest potential of polluting the receiving water. The nature and composition of industrial wastes widely vary from industry to an other and even within the same industry depending upon the raw materials, processes and operation factors. The industrial waste may have pollutants of almost all kinds ranging from simple nutrient and organic matter to complex toxic substances. The wastes from the industries like sugar factories, dairies, paper and pulp, tanneries, and distilleries are rich sources of organic matter. Metal plating industries release substantial quantities of heavy metals and cyanide in their wastes. The wastes from fertilizers industries can also be rich source of nutrients causing eutrophication. The chemical industry releases wastes with highly variable composition which are often acidic or alkaline in nature ^[1].

1.2 Electrochemical techniques

Electrochemistry is a scientific discipline with a well developed system of theories and quantitative relationships ^[25]. A number of important analytical methods are based on the electrochemical properties of solutions ^[26]. However, an electroanalytical method can be defined as one in which the electrical response of a chemical system or sample is measured.

Electrochemical methods can be divided into two classes:

Those involving ^[25], potentiometry which is the field of electroanalytical chemistry in which potential is measured under the conditions of no current

flow ^[27]. The measurement of electric potential in electrochemical cell, is probably one of the oldest methods of chemical analysis still in wide use. The early analytical applications of potentiometry were essentially to detect the end points of titration. More extensive use of direct potentiometric methods came after Haber developed the glass electrode for pH measurement in 1909. In recent years, several new classes of ion selective sensors have been introduced. In potentiometry, one measures the equilibrium thermodynamic potential of a system essentially without causing electrolysis or current drain on the system because this would affect the existing equilibrium ^[25]. Potentiometric methods are based on the measurement of a potential difference between two electrodes immersed in a solution ^[28].

The potential that develops in the electrochemical cell is the result of the free energy change that would occur in the chemical phenomena until the equilibrium condition has been satisfied ^[27].

In all other methods, a voltage or current is applied to an electrode and the resultant current flow through, or voltage change of, the system is monitored. Although this approach may be more complicated than the case in potentiometry. There are advantages in that one is not forced to deal with the particular equilibrium characteristics of the system.

1.2.1 Electrochemical cell

An electrochemical cell can be defined as two conductors or electrodes, may be metallic, immersed in the electrolyte solutions which are in electrical contact ^[25]. Electrochemical cells can be classified into two kinds: galvanic (or voltaic) and electrolytic. A galvanic cell consist of two electrodes immersed in one or more solutions (i.e., two half cells) and it is capable of spontaneously converting chemical energy more or less completely into

electrical energy and supplying this energy to an external source ^[29]. An electrolytic cell is one in which chemical reaction are caused to occur by the imposition of an external voltage greater than the reversible (galvanic) voltage of the cell ^[25]. Actually, a galvanic cell is built up from the products of the electrolytic cell that accumulate at the electrodes. When external current is turned off, the products tend to produce current in the opposite direction ^[29].

1.2.2 Ion Selective Electrode

Ion selective electrodes (ISE_s) are membrane electrodes that respond selectively to some ions in the presence of others ^[30]. It is based on passive membrane regions of space that separate two phases ^[31]. Ion selective electrode is one of the most frequently used potentiometric sensors during laboratory analysis as well as in industry, process control, physiological measurement, and environmental monitoring ^[32]. An ion-selective membrane is the key component of all potentiometric ion sensors. It establishes the preference with which the sensor responds to the analyte in the presence of various interfering ions from the sample ^[33] since some selective chemistry takes place at the surface of the electrode producing an internal potential. Species recognition is achieved with a potentiometric chemical sensor through a chemical equilibrium reaction at the sensor surface ^[34]. Ion selective electrodes which use such membrane were often referred to as being specific for a particular ion ^[35]. The term 'specific' implies that the electrode does not respond to additional ions. Since no electrode is truly specific for one ion, the term 'ion-selective' is recommended as more appropriate. 'Selective ion- sensitive electrode' is a little-used term to describe an ion-selective electrode. These include probes that measure specific ions and gases in solution. The most commonly used

ISE is the pH probe. Other ions that can be measured include element ions such as Fluoride, Bromide, Cadmium, Cupric and others, and gases in solution such as Ammonia, Carbon dioxide, nitrogen oxide, and Oxygen^[30]. Table(1-3) lists properties of some ion selective electrodes.

Table (1-3) shows some ion selective electrode and their characterization and parameters.

Characterization And parameters	Ion selective electrodes		
	calcium	copper	chloride
Slope	26±3	26±3	-54±5
Linear range(ppm)	0.1-4000	6.4x10 ⁻² - 6.4x10 ³	3-35000
Detection limit(ppm)	0.02	6.4x10 ⁻³	1
Response time(sec.)	10	10	10
Optimum temperature (°c)	25	25	25
pH range	3.5-11	2-7	1-12
Membrane type	Solid state PVC polymer matrix membrane	Solid state crystalline membrane	Solid state poly crystalline membrane
Ionic strength adjuster	4M KCl	5M NaNO ₃	5M NaNO ₃
Reference electrode	Single junction	double junction	double junction

1.2.2.1 General applications of ISE

Ion selective electrodes are now commercially available for the selective determination of large number of anions and cations and have found applications in many fields.

ISEs have been widely used for the evaluation of many equilibrium constants ^[36, 37], and reaction rates and mechanisms ^[38, 39]. Buff et al. ^[37] have described the use of silver chloride electrode to determine the solubility product, K_{sp} , of AgCl by direct calibration. The K_{sp} of AgCl was found to be $(1.9 \pm 0.04) \times 10^{-10}$ compared to literature value $(1.8 \times 10^{-10} \text{ mol}^2 \cdot \text{liter}^{-2})$.

The chemical composition of rocks and soils are of great importance in geology and agriculture studies. ISEs have been successfully employed to determine nitrate ^[40], fluoride ^[41], chloride ^[42], sulfide ^[43], sulfate ^[44], magnesium ^[45] and ammonium ^[46] in wide varieties of rocks, clays and soils. ISEs have been also used to measure oxides of nitrogen in air exhaust gases, and cigarette smoke ^[47]. Fluoride and chloride in rain and snow ^[48] hydrogen sulfide and cyanide in tobacco smock have been also determined by this method.

ISEs have been widely applied in paper pulp ^[49], liquors ^[50], metal plating ^[51], crude oil ^[52], explosives ^[53], and nuclear materials ^[54]. Overman ^[55] has reported a method for the determination of mercury (II), which is used as catalyst to dissolve aluminum in clad reactor fuel assemblies. In this process, Hg (II) has been removed before the reprocessed fuels are reclad because it would corrode new aluminum- clad fuels. The Hg (II) level is checked in the final solution by remote titration with iodine using iodide ion selective electrode.

ISEs have found wide biomedical applications. ISEs are the sole class of devices that have been fabricated for measuring important ions and dissolved gases in blood, such as calcium ^[56], fluoride ^[57], chloride ^[58], sodium ^[59], and ammonium ^[60]. Such devices respond to ion activities which are especially valuable in this field since life processes are related to activities and not to concentration. Corning sodium electrode ^[61] has been used in a flow through system for blood analysis. The electrode was found to have a high selectivity for Na⁺ over K⁺ ($K^{\text{POT. Na/K}} \sim 10^{-4}$).

ISEs can be used in the pollution monitoring such as cyanide, fluoride, copper, sulfide, chloride etc., in effluents and natural water ^[62].

1.2.2.2 Potentiometric measurement

The characterization of ion selective electrodes for a particular application has been based on the study of many parameters such as precision and accuracy and the time available to perform such analysis. The most important and widely used techniques for such studies are direct, standard addition, and titration methods ^[63]. The direct potentiometric measurement method is the most straightforward. The ISE and reference electrodes are immersed in the sample and the equilibrium cell potential is recorded. This method is extremely rapid, enabling measurements to be completed in two or three minutes. This method is suitable for the analysis of all samples in which the analyte of interest is present in the free uncomplexed state.

In standard addition method, the potential is first measured as in above then very small volume of standard solution of concentration higher than 100 times than sample concentration of the analyte is then added to the solution and the resulting potential is measured. This method based on the assumption that the activity coefficient of the analyte ion is identical before

and after the addition and that the degree of complexation of the analyte also remains constant throughout the measurement, since the volume of the analyte is relatively small ^[64].

The standard addition method is more applicable for the analysis of relatively complex matrix samples; in addition it is rapid and gives results that are more accurate for real samples in which interferent ions cause problems ^[64].

1.2.2.3 Ion analyses by ion selective electrode

Gavagnaro ^[65] has reviewed the electrochemical methods of water analysis. Two flow-through cupric selective electrode for the continuous and flow injection determination of cupric ion are described by Vander and Oostervink ^[66].

Stella and Ganzerli-Vanlentini ^[67] used a cupric ion selective electrode for the determination of inorganic copper species in fresh water.

Westall *et al* ^[68] studied the effect of chloride ion on cupric ion selective electrode measurements. On the basis of their method, the electrode was unsuitable for determination of cupric ion in sea water.

A number of suitable analytical techniques are available for the determination of chloride in water, including silver nitrate titration with chromate indicator ^[69], mercury (II) nitrate titration with diphenyl carbazone indicator, potentiometric titration with silver nitrate, automated iron(III) mercury (II) thiocyanate coulometry and ion selective electrode^[70].

Hulanicki and Trojanowica ^[71] have described the direct potentiometric determination of calcium in water with a constant complexation buffer.

Kawamura and Kashimu ^[72] described the determination of calcium and magnesium ions in the mixture by the electromotive force of calcium ion selective electrode and bivalent cation electrode.

Hu Z. *et al* ^[73] have described a direct potentiometric determination of water hardness with use of an ion selective electrode.

Grossmann *et al* ^[74] described a new method for measuring the hardness of water.

1.3 Atomic absorption spectroscopy

Atomic absorption spectroscopy is used for the qualitative and quantitative identification and determination of trace levels of metals in all types of materials and solutions ^[28]. The term atomic absorption refers to the absorption of energy from a light source, with consequent decrease in the radiant power transmitted through the flame ^[25].

1.3.1 General applications

Atomic absorption spectrophotometry has been used to determine metals and nonmetals in almost every conceivable type of sample. Many standard procedures for water analysis (river, ground, and lake water; sea water industrial effluents; beverage) has been based on AAS. Abundant elements (Na, K, Ca, Mg, and Fe) and many trace transition metals can usually be determined directly with flame AA. The use of AAS in metallurgical and mining industries is common for analysis of metals, alloys, geochemical samples and electroplating solutions. Flame AAS is adequate for determination of most elements at concentrations of 0.001% (w/w) or above in solid samples after dissolution by acids digestion or fusion.

Analysis of petroleum products presents special sample preparation difficulties. Oil and gasoline are often diluted by a factor of 2 to 10 with suitable solvents (heptane, xylene, methyl isobutyl ketone) so they can be aspirated into a flame.

For biological and clinical samples, it is critical to remove the organic matrix by digestion or some other method before analysis. With most biological samples, a flame ionization buffer is needed because of high content of Na and K ^[75].

1.3.2 Metal analyses by atomic absorption spectroscopy

Sturgeon *et al* ^[76] described a direct determination method for iron in water by graphite furnace atomic absorption spectroscopy.

Iron in water can be also determined by atomic absorption spectrometry (detection limit 5µg/liter) ^[77]. The average river iron concentration has been reported to be 0.7 mg/L ^[78].

Fishman and Downs ^[79] have described a method for determination of calcium, copper, lithium, magnesium, manganese, potassium, sodium, strontium and zinc in natural water and may be applicable to other elements by atomic absorption spectroscopy.

Air-acetylene flame atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) emission spectroscopy have been used for determination of calcium in water. The detection limit of the AAS method on direct aspiration is 3 µg/L, and the optimum concentration range from (0.2 to 20 mg/L). The recovery of added calcium in a spiked sample is between 85 and 115 percent ^[80].

Dawson and Heaton ^[81] have described a method to the determination of magnesium in biological materials by atomic absorption spectrophotometry.

Atomic absorption spectroscopy is a suitable method for the determination of As, Pb and Hg in part per million and sub-part per billion levels in environmental and biological samples as described by Gautam *et al* ^[82]. In this work the analysis of various environmental and biological samples were investigated. This technique is fast simple and highly sensitive. The

detection limit of As, Pb and Hg were 1.8 $\mu\text{g/L}$, 1.6 $\mu\text{g/L}$ and 1.5- 1.6 $\mu\text{g/L}$ respectively.

Taher ^[83] has described method to the determination of trace lead after solid liquid extraction and preconcentration using 1-(2- pyridylazol-2-naphthol). The extraction of metal from water samples by a chelating agent was reported to selectivity extract heavy metals.

Dingman *et al* ^[84], have reported a concentration factor as high as 1000 when using poly urea resin to extract Cu, Zn, Ni and Co. These metals were then determined by atomic absorption spectroscopy.

Many atomic spectrometric methods had been reported ^[85], for the determination of metal ions concentration of different samples. These methods were used for determination the concentration of the sample metal components by ion exchange process followed by emission spectrophotometry were reported by Thomas ^[86].

1.4 Aim of the work

The aim of this work was to evaluate the water quality in some Iraqi water resources (tap, river and ground water), in different governorates (**Al-Sulaimaniyah, Al- Mosul, Diyala, Baghdad, Karbala, Al- Najaf and Al-Diwaniyah**).

The study concern with determination of (calcium, magnesium, chloride, copper, iron, and lead) metal ions concentration. Some of these ions may be toxic for human and other organisms if their concentrations were above the maximum level.

3. Results and discussion

3.1 Quantitative analysis using ion selective electrodes

- Calcium

A linear calibration curve was obtained extended from (1 -1000) ppm, as shown in figure (3-1) with line equation of

$$y = 30.259 \text{ Log } x + 33.823 \dots\dots (3-1)$$

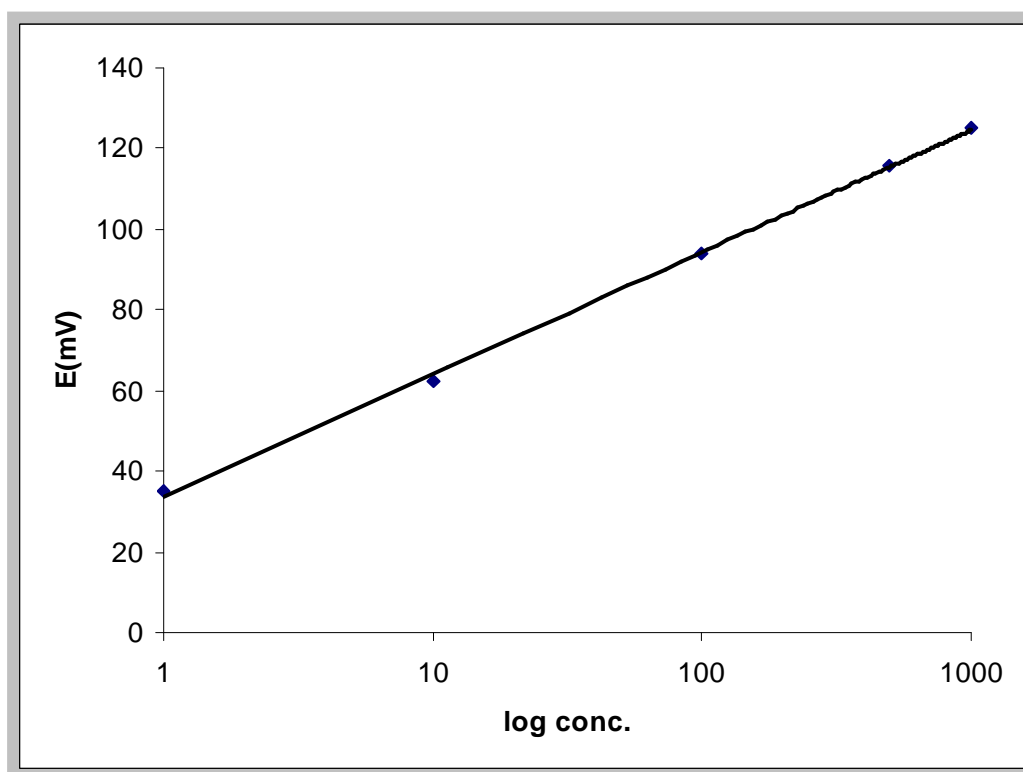


Fig (3-1) calibration of calcium ion selective electrode

Where y represents the potential value (mV) and the x represents the log of the concentration for the calcium ion.

The correlation factor for this line was 0.9995 with a relative standard deviation of 0.0929%.

The slope of this calibration curve was 30.259 which nearly represent the slope of calcium ion selective electrode as shown in table (1-3).

The concentration of calcium in different water samples was determined by multiple standard addition method, and the results were tabulated in table (3-1).

Table (3-1) Calcium concentration determined by ion selective electrode in different water samples in Iraq

location	Concentration of calcium (ppm) \pm SD*		
	Tap water	River water	Ground water
Sulaimaniyah	20.73 \pm 0.05		32.42 \pm 0.08
Mosul	27.16 \pm 0.15	Tigris rver	
		39.19 \pm 0.07	
Diyala	29.89 \pm 0.08	43.21 \pm 0.06	
Baghdad (Qadissyah Q.)	23.16 \pm 0.12	50.81 \pm 0.05	55.08 \pm 0.09
			58.79 \pm 0.07
Baghdad (Dora Q.)	26.45 \pm 0.12		
Karbala	30.56 \pm 0.11	Euphrates river	
		55.22 \pm 0.09	
Najaf	39.89 \pm 0.10	62.38 \pm 0.12	
Diwaniyah	44.66 \pm 0.15	73.19 \pm 0.1	

* Each reading was an average of three measurements

The average SD for these samples was \pm 0.0946.

The calcium concentration was in the range (20.73 to 44.66) ppm for tap water, and in the range (39.19 to 73.19) ppm in river water.

From table (3-1) the governorates which lie at both rivers (Tigris and Euphrates) it was found that the lowest level of calcium concentration for tap water was in **Al-Sulaimaniyah**, and the highest level of calcium concentration in both rivers and tap water was found in **Al- Diwaniyah**.

And the lowest calcium concentration in Tigris and Euphrates rivers was found in **Al-Mosul** and the highest level was found in **Al- Diwaniyah** for river water.

Also from the above table the concentration of calcium in river was found to be higher than its concentration in tap water for each governorates lie at Tigris and Euphrates rivers, and for **Baghdad** the concentration of calcium in ground water is higher than its concentration in river, because surface water generally contains lower concentration of calcium than ground water ^[88], and the last has a higher calcium concentration than in tap water, and for **Al- Sulaimaniyah** the concentration of calcium in the ground water was higher than its concentration in the tap water. That because calcium is primarily found in ground water due to the dissolving of limestone (calcium carbonate) the dissolving occurs when the limestone reacts with rain water which has become slightly acidic through a reaction with carbon dioxide ^[2].

However, for Tigris the concentration of calcium increased from the north down to south of the direction of the river for both tap and river water except **Baghdad (Qadissyah Q.)** and **al Dora** tap water which has lower concentration than **Al- Mosul** and **Diyala**, and for Euphrates the concentration of calcium were found to be increased from the north down to the south of the river direction. The calcium concentration in both tap and river water in Tigris was found to be lower than its concentration in Euphrates. The calcium distributions was shown in figure (3-2)

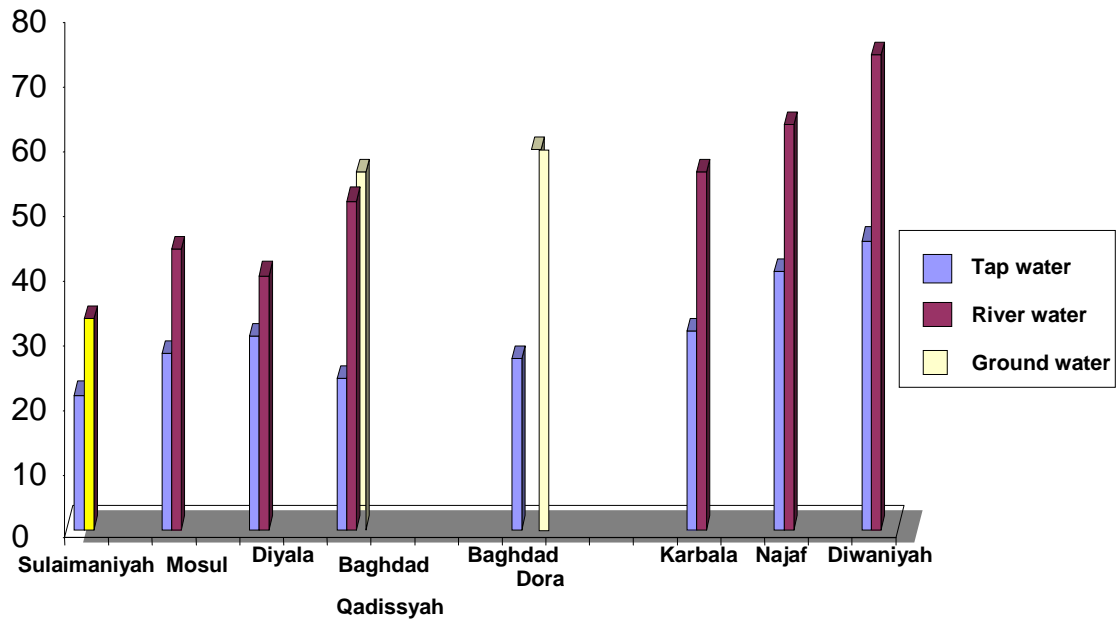


Fig (3-2) calcium distribution in tap, river and ground water measured by ion selective electrode

• Copper

A linear calibration curve was obtained extended from (0.1 -1000) ppm, as shown in figure (3-3) with line equation of

$$y = 29.75 \text{ Log } x + 214.99 \dots \dots (3-2)$$

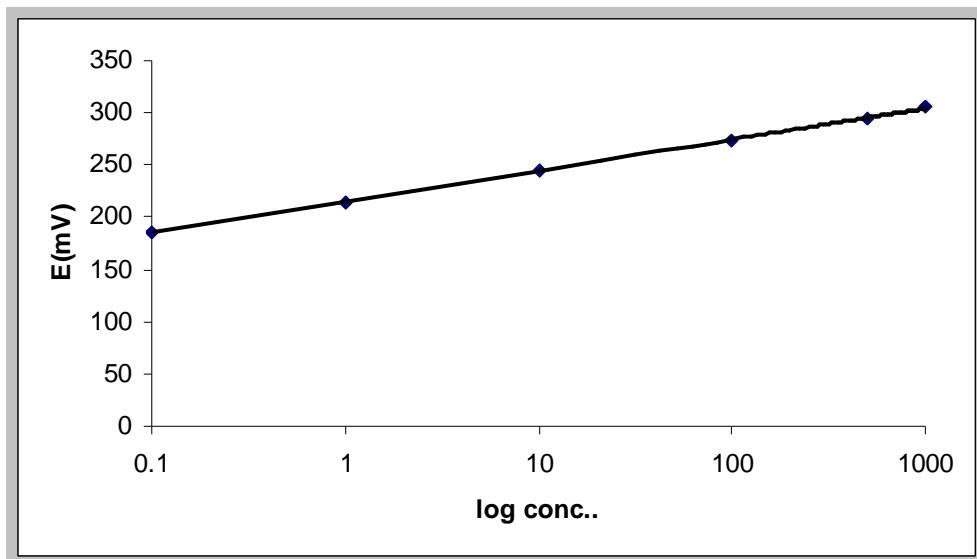


Fig (3-3) calibration of cupric ion selective electrode

Where y represents the potential value (mV) and the x represents the log of the concentration of cupric ion.

The correlation factor for this line was 0.9996 with a relative standard deviation 0.0282%.

The slope of this calibration curve was 29.75 which nearly represent the slope of cupric ion selective electrode as shown in table (1-3).

The concentration of copper in different water samples was determined by multiple standard addition method, and the results were tabulated in table (3-2).

Table (3-2) Copper concentration determined by cupric ion selective electrode in different water samples in Iraq

location	Concentration of copper (ppm) \pm SD*		
	Tap water	River water	Ground water
Sulaimaniyah	0.053 \pm 0.005		0.035 \pm 0.001
Mosul	0.064 \pm 0.003	Tigris river	
		0.036 \pm 0.007	
Diyala	0.085 \pm 0.002	0.044 \pm 0.001	
Baghdad (Qadissyah Q.)	0.071 \pm 0.001	0.045 \pm 0.002	0.049 \pm 0.004
Baghdad (Dora Q.)	0.072 \pm 0.003		0.058 \pm 0.002
Karbala	0.082 \pm 0.001	Euphrates river	
		0.063 \pm 0.005	
Najaf	0.096 \pm 0.004	0.066 \pm 0.004	
Diwaniyah	0.105 \pm 0.005	0.069 \pm 0.001	

*Each reading was an average of three measurements

The average SD for these samples was ± 0.0029 . The copper concentration was in the range (0.053 to 0.105) ppm for tap water, and in the range (0.036 to 0.069) ppm in river water.

From table (3-2) for both Tigris and Euphrates rivers the lowest level of copper concentration for tap water was found in **Al- Sulaimaniyah**, and the highest level of copper concentration in tap water was found in **Al-Diwaniyah**.

For river water the highest level of copper concentration was found in **Al-Diwaniyah**, while the lowest level was found in **Al- Mosul**. For **Baghdad** the copper concentration in the ground water was higher than copper concentration in the river but has a lower concentration than in the tap water and in **Al- Sulaimaniyah** the copper concentration in the ground water was lower than its concentration in the tap water.

Generally from table (3-2), for Tigris and Euphrates the concentration of copper in the river water was relatively lower than its concentration in the tap water for each governorate. This is because of the main source of copper in the drinking water comes from the corrosion of the pipes.

However, for governorates which lie at Tigris the concentration of copper in the tap water increases from the north down to the south of the river direction except **Diyala** which has copper concentration higher than **Baghdad**. The copper concentration in river water has also increases from the north down to the south Tigris direction. And for the governorates lie at Euphrates the copper concentration in the tap and river water have also increases from the north down to the south of the river direction. However, the copper concentration in both tap and river water for the governorates which lie at Tigris was lower than its concentration in governorates lies at al Euphrates except **Diyala** which has copper concentration higher than **Karbala**. The distribution of copper ion in water samples were shown in figure (3-4).

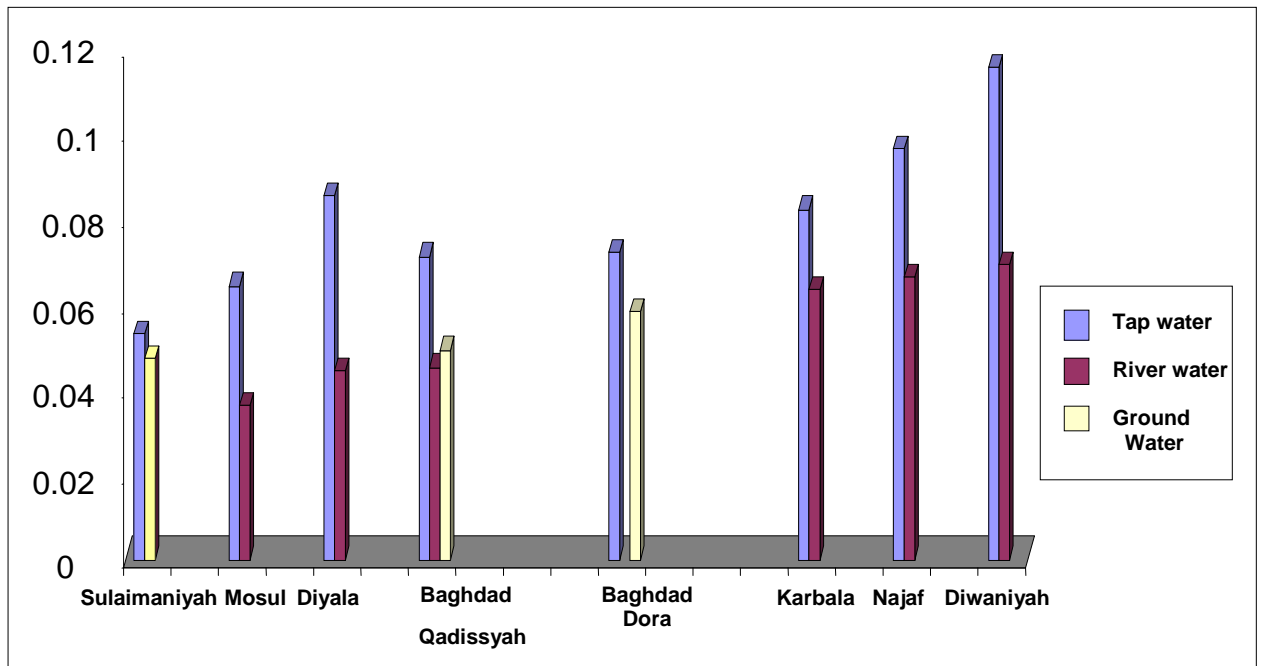


Fig (3-4) copper distribution in tap, river and ground water measured by ion selective electrode

- **Chloride**

A linear calibration curve was obtained extended from (1 -1000) ppm, as shown in figure (3-5) with line equation of

$$y = -57.05 \text{ Log } x + 68.246 \dots \dots (3-3)$$

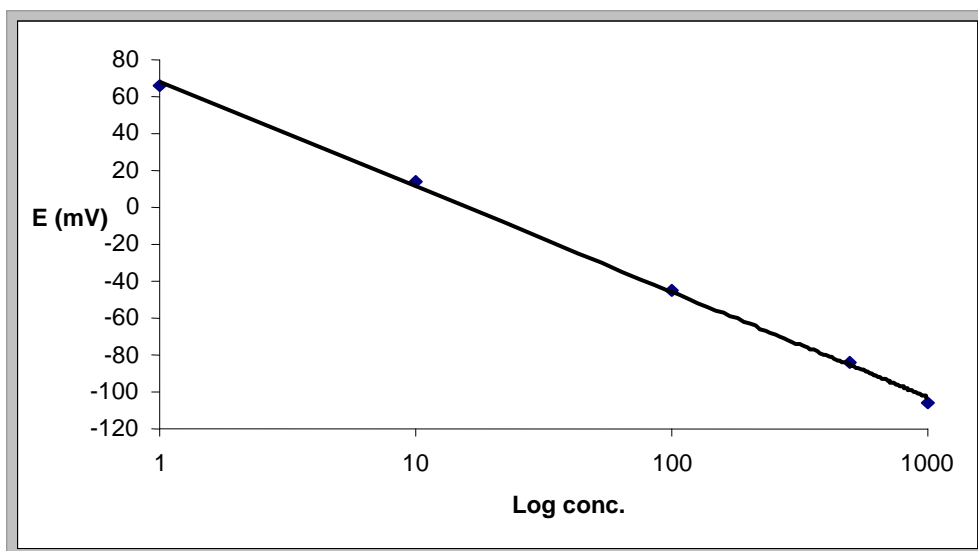


Fig (3-5) calibration of chloride ion selective electrode

Where y represents the potential value (mV) and the x represents the log of the concentration of chloride ion.

The correlation factor was 0.9993 with a relative standard deviation of 0.136%.

The slope of this calibration curve was -57.05 which represent the slope of chloride ion selective electrode as shown in table (1-3).

The concentration of chloride in different water samples was determined by multiple standard addition method, and the results were tabulated in table (3-3).

Table (3-3) Chloride concentration determined by chloride ion selective electrode in different water samples in Iraq

location	Concentration of chloride (ppm) \pm SD*		
	Tap water	River water	Ground water
Sulaimaniyah	167.04 \pm 0.09		148.61 \pm 0.03
Mosul	251.33 \pm 0.09	Tigris river	
		216.81 \pm 0.06	
Diyala	298.32 \pm 0.18	280.45 \pm 0.16	
Baghdad (Qadissyah Q.)	246.37 \pm 0.21	225.18 \pm 0.09	199.71 \pm 0.06
Baghdad (Dora Q.)	299.59 \pm 0.14		209.45 \pm 0.12
Karbala	316.88 \pm 0.07	Euphrates river	
		344.08 \pm 0.09	
Najaf	327.61 \pm 0.09	416.29 \pm 0.09	
Diwaniyah	370.01 \pm 0.12	433.75 \pm 0.21	

*Each reading was an average of three measurements

The average SD for these samples was \pm 0.108.

The chloride ion concentration was in the range (167.04 to 370.01) ppm for tap water, and in the range (216.81 to 433.75) ppm in river water for the governorates which lie at Tigris and Euphrates rivers.

From table (3-3) the lowest level of chloride concentration for both Tigris and Euphrates for the tap water is found in **Al- Sulaimaniyah**, and the highest level of chloride concentration of tap water is found in **Al-Diwaniyah**, for river water the lowest chloride concentration was found at **Al- Mosul** and the highest level of chloride concentration in river water was also found in **Al- Diwaniyah**. In **Baghdad** the chloride concentration in the ground water was found to be lower than its concentration in the river and tap water as same as in **Al- Sulaimaniyah**.

For the governorates which lie at Tigris the concentration of chloride in the tap water was higher than its concentration in the river water, but for the governorates which lie at Euphrates the concentration of chloride in the tap water is lower than its concentration in the river water.

For governorates which lies at Tigris for the tap and river water the chloride concentration increases from the north down to the south of the river direction but the chloride concentration in **Baghdad (Qadissyah Q.)** was lower than chloride in **Diyala** for both tap and river water. The same as in the governorates which lie at Euphrates the chloride concentration increases from the north down to the south of the river direction. However, the chloride concentration for tap and river water of the governorates position at the Tigris river were found to be lower than the chloride concentration for the governorates position at Euphrates.

The chloride ion distribution in Iraqi governorates for tap, river and ground water were shown in figure (3-6)

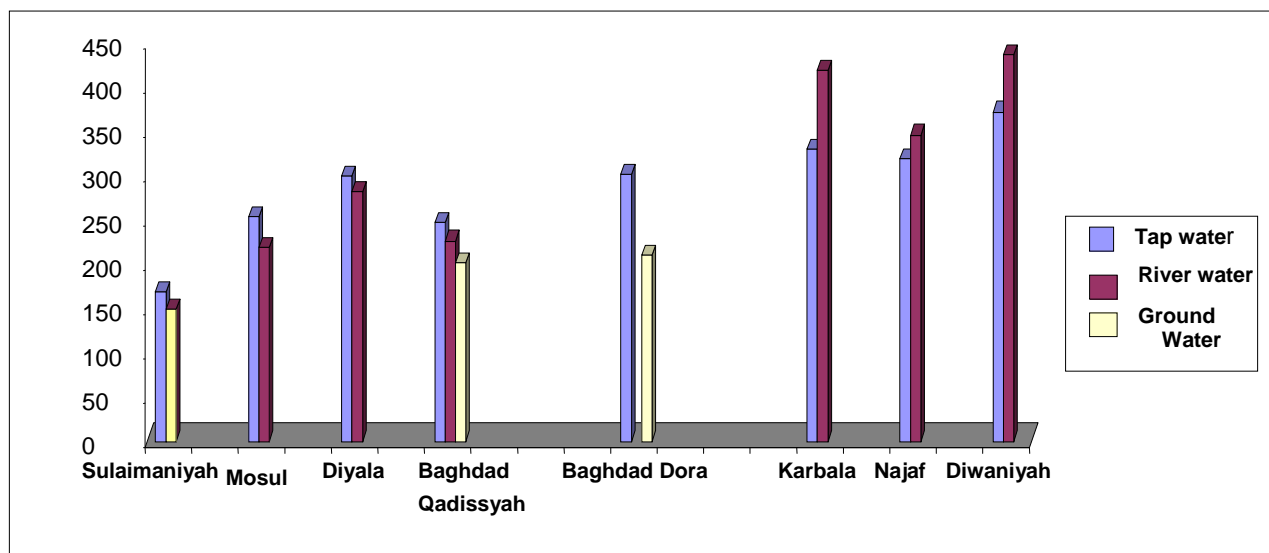


Fig (3-6) chloride distribution in tap, river and ground water measured by ion selective electrode

For the ions which determined by ion selective electrode the recovery and error were tabulated in the table (3-4)

Table (3-4) Recovery of the ions measured 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

Where the chloride has the highest recovery 99.31 followed by calcium which has recovery of 98.12 and at last copper which has the lowest recovery of 97.15.

3.2 Quantitative analysis using atomic absorption spectroscopy

- **Iron**

A calibration curve was constructed for iron employing 248.3 nm as absorption line for the metal.

A linear calibration curve was obtained extended from (0.1-10) ppm, as shown in figure (3-7) with equation of

$$y = 0.0584x - 0.0015 \dots \dots (3-4)$$

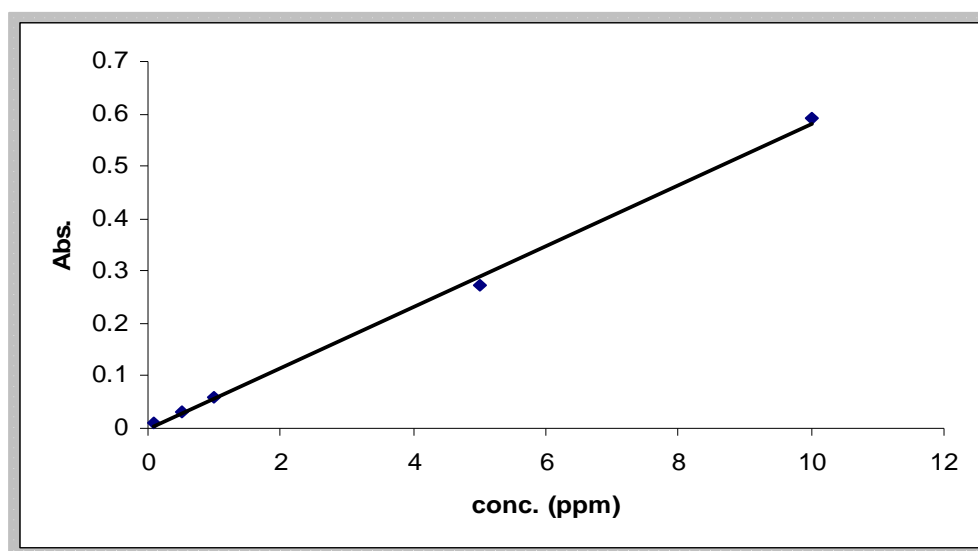


Fig. (3-7) calibration curve of iron

Where y represents the absorbance value and x represents the concentration of iron.

The correlation factor for this line was 0.9991 with a relative standard deviation of 1.624%.

The concentration of iron in different types of water samples was calculated using the above linear equation (3-4), and the results are tabulated in table (3-5).

Table (3-5) Iron concentration determined by atomic absorption in different water samples in Iraq

location	Concentration of iron (ppm) in \pm SD*		
	Tap water	River water	Ground water
Sulaimaniyah	0.135 \pm 0.003		0.095 \pm 0.01
Mosul	0.178 \pm 0.005	Tigris river	
		0.127 \pm 0.01	
Diyala	0.182 \pm 0.003	0.139 \pm 0.01	
Baghdad (Qadissyah Q.)	0.191 \pm 0.005	0.145 \pm 0.003	0.038 \pm 0.004
Baghdad (Dora Q.)	0.198 \pm 0.001		0.078 \pm 0.004
Karbala	0.206 \pm 0.004	Euphrates river	
		0.157 \pm 0.003	
Najaf	0.211 \pm 0.01	0.188 \pm 0.02	
Diwaniyah	0.273 \pm 0.002	0.221 \pm 0.005	

*Each reading was an average of three measurements
The average SD for these samples was of ± 0.0026

The iron concentration was in the range (0.135 to 0.273) ppm for tap water, and in the range (0.127 to 0.247) ppm in river water.

From table (3-5) the lowest iron concentration in governorates that lies at Tigris and Euphrates rivers for tap water was found in **AL-Sulaimaniyah**, while the highest iron concentration for tap water was found in **AL-Diwaniyah**. The lowest iron concentration was found in both rivers were found in **Al-Mosul** while the highest concentration was found in **AL-Diwaniyah** river water.

For **Baghdad** the concentration of iron in the ground water was lower than its concentration in the tap and river water, and in **AL-Sulaimaniyah** the iron concentration in ground water was lower than its concentration in the tap water. Most ground water has at least trace amount of iron because its presence in nature is so common [2].

Iron concentration in both Tigris and Euphrates rivers were found to be lower than iron concentration in tap water, that because the source of iron in drinking water may come from the corrosion of pipes.

For both governorates which lie at Tigris and Euphrates rivers the iron concentrations in tap and river water were increased from the north down to the south of the rivers directions. However, the iron concentration for the governorates which lies at Tigris River in tap and river water was found to be lower than its concentration in the governorates which lies at Euphrates. The iron distribution in water samples is shown in figure (3-8).

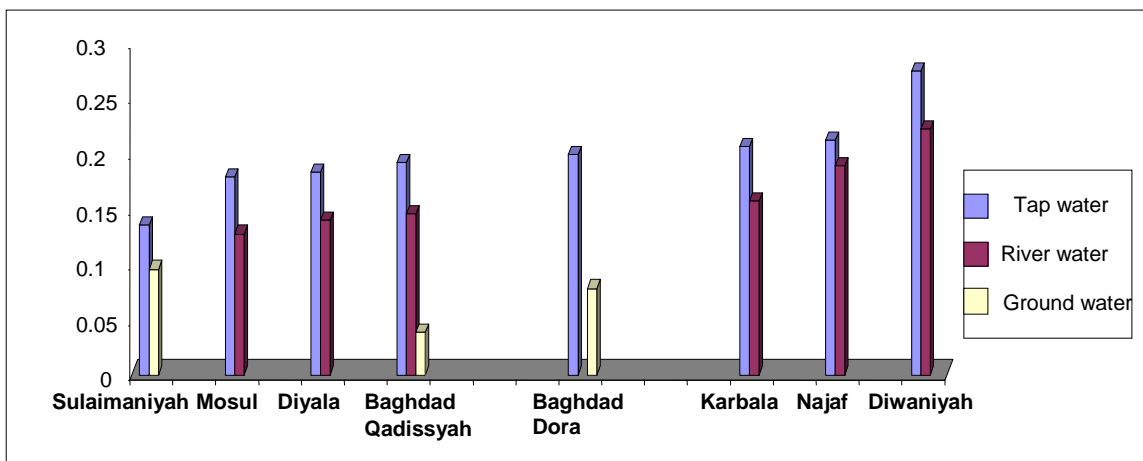


Fig (3-8) Iron distribution in tap, river and ground water measured by atomic absorption

- **Lead**

A calibration curve was constructed for lead employing 283.8 nm as absorbing line for the metal.

A linear calibration curve was obtained extended from (0.01-10) ppm, as shown in figure (3-9) with equation of

$$y = 0.243 x - 0.0068 \dots \dots (3-5)$$

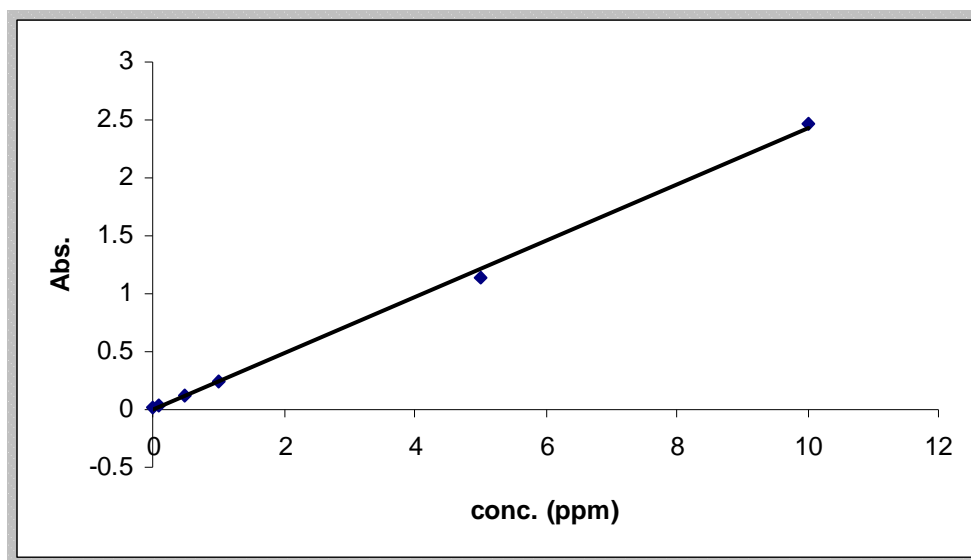


Fig. (3-9) calibration curve of lead

Where y represents the absorbance value and x represents the concentration of lead.

The correlation factor for this line was 0.9992 with a relative standard deviation 3.144%.

The concentration of lead in different types of water samples was calculated using the above linear equation (3-5), and the results were tabulated in table (3-6).

Table (3-6) Lead concentration determined by atomic absorption in different water samples in Iraq

location	Concentration of lead (ppm) \pm SD*		
	Tap water	River water	Ground water
Sulaimaniyah	nil		nil
Mosul	nil	nil	
Diyala	$0.0103 \pm 9 \times 10^{-4}$	nil	
Baghdad (Qadissyah Q.)	$0.008 \pm 8 \times 10^{-4}$	nil	nil
Baghdad (Dora Q.)	$0.011 \pm 5 \times 10^{-4}$		nil
Karbala	$0.0099 \pm 7 \times 10^{-4}$	nil	
Najaf	$0.012 \pm 9 \times 10^{-4}$	nil	
Diwaniyah	$0.013 \pm 5 \times 10^{-4}$	nil	

*Each reading was an average of three measurements
The average SD for these samples was ± 0.000705 .

The detected lead concentration in tap water was in the range (0.008 to 0.013) ppm, and there was no detection of lead in the river water or in the ground water in all water samples.

That's because lead is rarely occurs in naturally in drinking water resources, but results from the corrosive action of water on materials used in the distribution and plumping system. The U.S. environmental

protection agency (EPA) estimated that 20% of our total lead exposure comes from drinking water ^[8]. The lowest lead concentration for governorates which lies at both Tigris and Euphrates rivers was found in **Baghdad (Qadissyah Q.)** and the highest detection of lead was found in **Al- Diwaniyah**.

The detected lead concentration distribution in tap water is shown in figure (3-10)

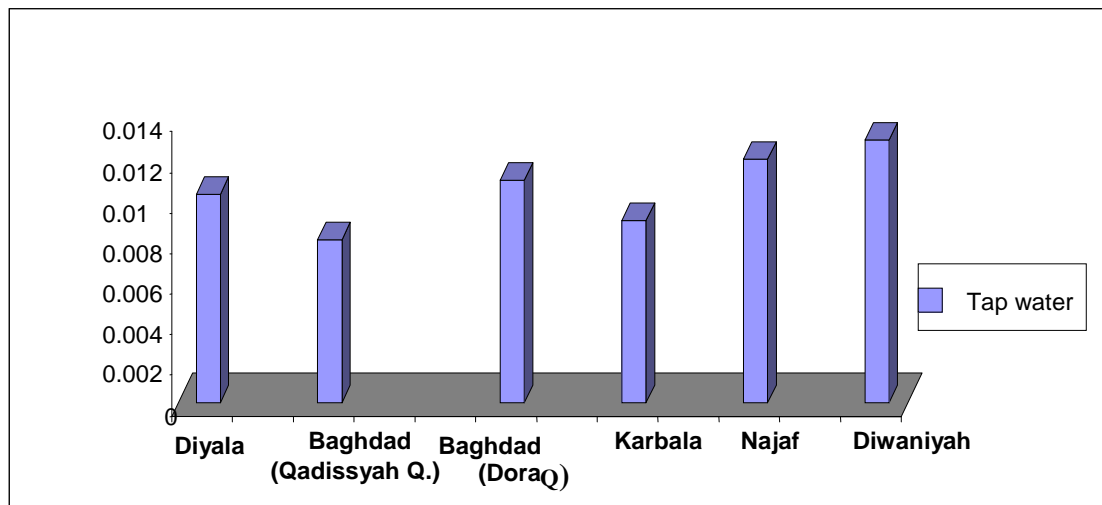


Figure (3-10) Lead distribution in tap water measured by atomic absorption

- **Copper**

A calibration curve was constructed for copper employing 324.8 nm as absorption line for the metal.

A linear calibration curve was obtained extended from (0.01-10) ppm, as shown in figure (3-11) with equation of

$$y = 0.0853x - 0.0079 \dots \dots (3-6)$$

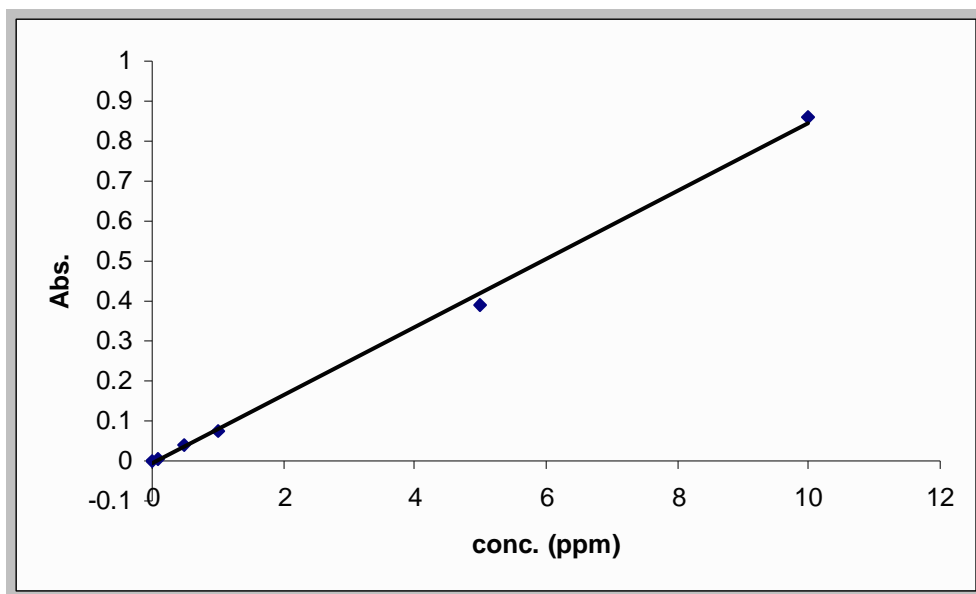


Fig (3-11) calibration curve of copper using AAS

Where y represents the absorbance value and x represents the concentration of copper.

The correlation factor for this line was 0.9989 with a relative standard deviation 1.59 %.

The concentration of copper in different types of water samples was calculated using the above linear equation (3-6), and the results were tabulated in table (3-7).

Table (3-7) Copper concentration determined by atomic absorption in different water samples in Iraq

Location	Concentration of copper (ppm) \pm SD*		
	Tap water	River water	Ground water
Sulaimaniyah	0.054 \pm 0.004		0.039 \pm 0.007
Mosul	0.073 \pm 0.004	Tigris river	
		0.042 \pm 0.007	
Diyala	0.082 \pm 0.006	0.047 \pm 0.004	
Baghdad (Qadissyah Q.)	0.076 \pm 0.004	0.051 \pm 0.003	0.053 \pm 0.004
Baghdad (Dora Q.)	0.088 \pm 0.002		0.061 \pm 0.005
Karbala	0.091 \pm 0.008	Euphrates river	
		0.065 \pm 0.001	
Najaf	0.098 \pm 0.001	0.069 \pm 0.003	
Diwaniyah	0.12 \pm 0.002	0.071 \pm 0.001	

*Each reading was an average of three measurements

The average SD for these samples was \pm 0.00371.

The copper concentration was in the range (0.054 to 0.12) ppm for tap water, and in the range (0.039 to 0.071) ppm in river water.

From table (3-7) the lowest copper concentration level for governorates which lie at both Tigris and Euphrates rivers for tap water was found in **AL-Sulaimaniyah** and the highest was found in **Al- Diwaniyah**. And the lowest copper concentration in Tigris and Euphrates river water was found in **Al- Mosul**, while the highest was also found in **Al- Diwaniyah**.

In Baghdad the concentration of copper in the ground water was found to be lower than its concentration in tap water but higher than river water. **AL-Sulaimaniyah** ground water has lower copper concentration than in the tap water.

However, the concentration of copper in both Tigris and Euphrates rivers were lower than its concentration in the tap water.

The copper concentration in the tap and river water for the governorates which lie at Euphrates was higher than its concentration for the governorates lies at Tigris. The governorates which lie at Tigris were found that their copper concentration increased from the north down to south with an exception that concentration of copper in **Baghdad (Qadissyah Q.)** was found to be lower than its concentration in **Diyala**. The governorates which lie at Euphrates were found that the copper concentration increased from the north down to south for both river and tap water. The copper distribution in water samples measured using AAS is shown in figure (3-12).

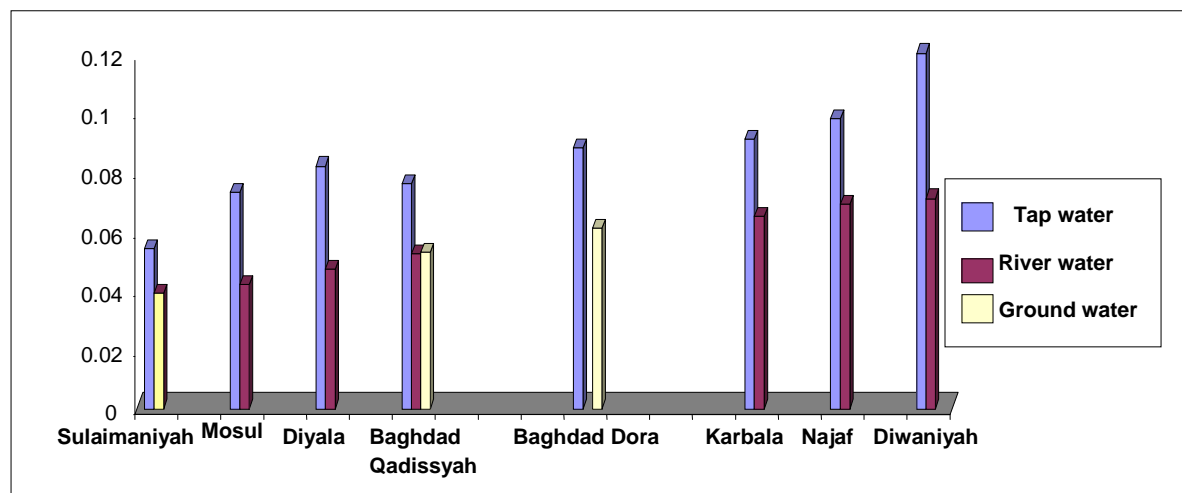


Fig (3-12) Copper distribution in tap, river and ground water measured by atomic absorption.

- **Magnesium**

A calibration curve was constructed for magnesium employing 285.2 nm as absorption line for the metal.

A linear calibration curve was obtained extended from (1-100) ppm, as shown in figure (3-13) with equation of

$$y = 0.8388 x - 0.6867 \dots\dots (3-7)$$

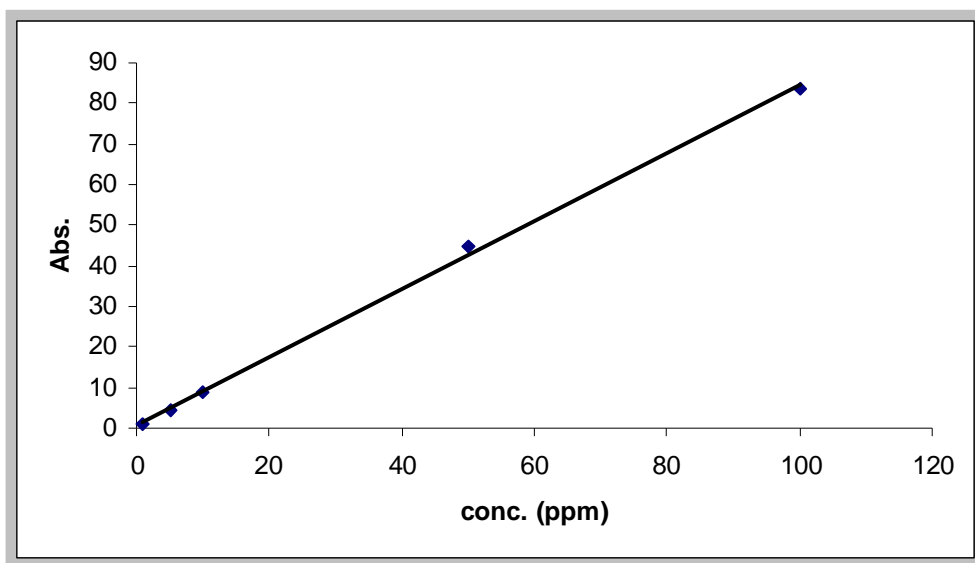


Fig (3-13) calibration curve of magnesium

Where y represents the absorbance value and x represents the concentration of magnesium.

The correlation factor for this line was 0.9993 with a relative standard deviation of 0.0195 %.

The concentration of magnesium in different types of water samples was calculated using the above linear equation (3-7), and the results are tabulated in table (3-8).

Table (3-8) Magnesium concentration in different water samples in Iraq

Location	Concentration of magnesium (ppm) \pm SD*		
	Tap water	River water	Ground water
Sulaimaniyah	7.87 \pm 0.05		15.53 \pm 0.05
Mosul	13.46 \pm 0.17	Tigris river	
		18.53 \pm 0.04	
Diyala	14.21 \pm 0.13	20.54 \pm 0.10	
Baghdad (Qadissyah Q.)	9.53 \pm 0.12	24.56 \pm 0.12	22.25 \pm 0.3
Baghdad (Dora Q.)	12.23 \pm 0.11		23.09 \pm 0.10
Karbala	16.87 \pm 0.06	Euphrates river	
		25.44 \pm 0.05	
Najaf	17.65 \pm 0.09	29.71 \pm 0.07	
Diwaniyah	18.91 \pm 0.07	33.33 \pm 0.18	

*Each reading was an average of three measurements

The average SD for these samples was \pm 0.105. The magnesium concentration was in the range (7.87 to 18.91) ppm for tap water, and in the range (18.53 to 33.33) ppm in river water.

From table (3-8) the lowest magnesium concentration levels was found in governorates which lie at both Tigris and Euphrates rivers and for tap water in **Al-Sulaimaniyah** and the highest magnesium concentration were found in **Al- Diwaniyah**. The lowest level of magnesium concentration in both Tigris and Euphrates was found in **Al- Mosul** while the highest concentration found in **Al- Diwaniyah**.

In **Baghdad** the concentration of magnesium in the ground water was found to be higher than its concentration in tap water but lower than in river water and in **AL-Sulaimaniyah** the ground water has higher magnesium concentration than in tap water. The concentration of magnesium in both Tigris and Euphrates rivers were higher than its concentration in tap water.

The governorates which lie at Tigris was found that the magnesium concentration in both tap and river water increased from the north down to south of the river direction, with an exception in **Baghdad (Qadissyah Q.)** and **Al Dora** which were found to be lower than its concentration in **Diyala** and **Al Mosul**.

The governorates which lie at Euphrates were found that the magnesium concentration increased from the north down to south of the river direction for both river and tap water. However, the concentration of magnesium for both tap and river water in Euphrates was found to have higher concentration than in Tigris. The magnesium distribution in the tap, river and ground water are shown in figure (3-14).

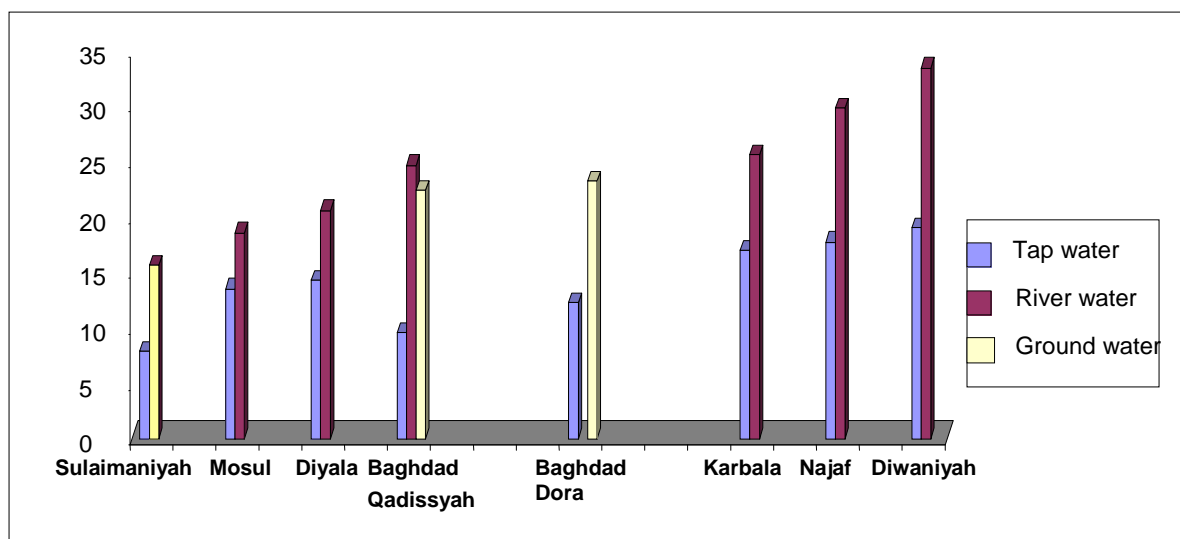


Fig (3-14) Magnesium distribution in tap, river and ground water measured using atomic absorption.

- **Calcium**

A calibration curve was constructed for calcium employing 422.5 nm as absorption line for the metal.

A linear calibration curve was obtained extended from (1-100) ppm, as shown in figure (3-15) with equation of

$$y = 0.6127 x - 0.5464 \dots \dots (3-8)$$

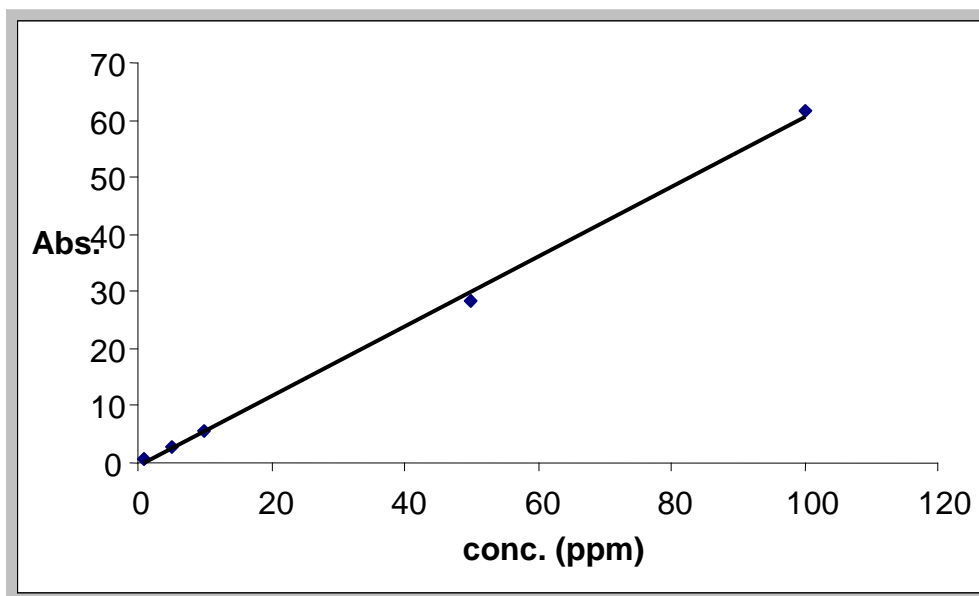


Fig (3-15) calibration curve of calcium using AAS

Where Y represents the absorbance value and x represents the concentration of calcium.

The correlation factor for this line was 0.9991 with a relative standard deviation of 3.57 %.

The concentration of calcium in different types of water samples was calculated using the above linear equation (3-8), and the results are tabulated in table (3-9).

Table (3-9) Calcium concentration determined by atomic absorption in different water samples in Iraq

Location	Concentration * of calcium (ppm) \pm SD		
	Tap water	River water	Ground water
Sulaimaniyah	21.05 \pm 0.12		32.91 \pm 0.38
Mosul	27.85 \pm 0.15	Tigris river	
		39.39 \pm 0.35	
Diyala	30.35 \pm 0.29	43.87 \pm 0.23	
Baghdad (Qadissyah Q.)	22.82 \pm 0.044	55.93 \pm 0.14	56.58 \pm 0.17
Baghdad (Dora Q.)	26.86 \pm 0.13		59.69 \pm 0.72
Karbala	30.69 \pm 0.11	Euphrates river	
		56.07 \pm 0.15	
Najaf	39.28 \pm 0.09	63.51 \pm 0.19	
Diwaniyah	45.23 \pm 0.07	73.37 \pm 0.06	

*Each reading was an average of three measurements

The average SD for these samples was \pm 0.253.

The calcium concentration was in the range (21.05 to 45.23) ppm for tap water, and in the range (39.39 to 73.37) ppm in river water.

From table (3-9) the lowest calcium concentration level for governorates which lies at both Tigris and Euphrates Rivers for tap water was found in **AL-Sulaimaniyah** and the highest calcium concentration were found in **Al- Diwaniyah**. The lowest calcium concentration in Tigris and

Euphrates were found in **AL-Mosul**, while the highest level was found also in **Al- Diwaniyah**.

In **Baghdad** the concentration of calcium in the ground water was found to be higher than its concentration in tap water and river water, and **AL-Sulaimaniyah** ground water has higher calcium concentration than in tap water. The concentration of calcium in both Tigris and Euphrates rivers were found to be higher than its concentration in tap water.

The governorates which lie at Tigris were found that their calcium concentration in both tap and river water increased from the north down to south of the river direction, with an exception in **Baghdad (Qadissyah Q.)** and **Al Dora** was found to be lower than its concentration in **Diyala** and **Al Mosul**.

The governorates which lie at Euphrates were found that the calcium concentration increased from the north down to south of the river direction in both river and tap water. However, the concentration of calcium for both tap and river water in Euphrates was found to have higher concentration than in Tigris. The calcium measured by AAS distribution in the water samples are shown in figure (3-16).

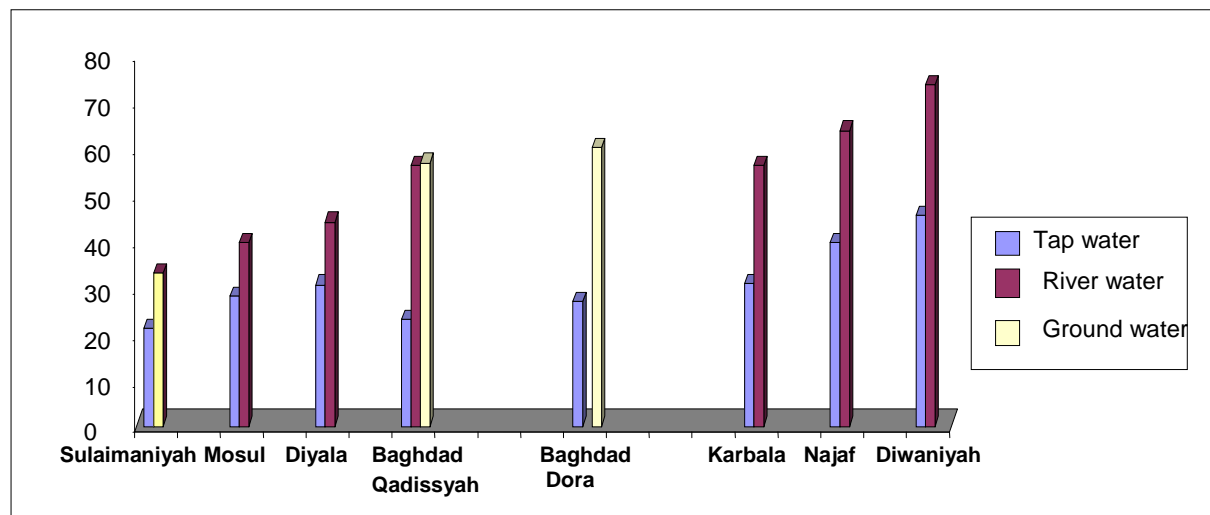


Fig (3-16) Calcium distribution in tap, river and ground water measured by atomic absorption.

For the atomic absorption measurements the recovery and error was obtained for the standard of metals has been tabulated in table (3-10).

Table (3-10) Recovery and relative error for standard of metals measured by AAS

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

From table (3-10) the metals measured by atomic absorption the highest recovery was obtained for magnesium 99.5 followed by iron 98.67 and calcium 98.47 and copper 98.34 and the lowest recovery for these metals was found for lead 97.98

The recovery of calcium and copper measured by atomic absorption was higher than the recovery of the same metals measured by ion selective electrode which was for copper 97.15 and for calcium was 98.13.

3.3 Quantitative chloride determinations by titration

The chloride concentration was directly determined in water samples by titration with silver nitrate, and the results were tabulated in table (3-11).

Table (3-11) Chloride concentration determined by titration with AgNO_3 in different water samples in Iraq

Location	Concentration * of chloride (ppm) \pm SD		
	Tap water	River water	Ground water
Sulaimaniyah	161.34 \pm 0.18		153.77 \pm 0.45
Mosul	242.88 \pm 0.62	Tigris river	
		210.34 \pm 0.192	
Diyala	308.69 \pm 0.19	271.02 \pm 0.04	
Baghdad (Qadissyah Q.)	238.09 \pm 0.16	219.25 \pm 0.02	192.99 \pm 0.16
Baghdad (Dora Q.)	289.52 \pm 0.02		207.41 \pm 0.02
Karbala	305.14 \pm 0.25	Euphrates river	
		356.04 \pm 0.02	
Najaf	316.58 \pm 0.54	402.44 \pm 0.22	
Diwaniyah	357.57 \pm 0.29	419.17 \pm 0.27	

*Each reading was an average of three measurements

The average SD for these samples was \pm 0.215.

The chloride ion concentration was in the range (161.34 to 357.57) ppm for tap water, and in the range (210.4 to 419.17) ppm in river water for the governorates lie at Tigris and Euphrates rivers.

From table (3-11) the lowest level of chloride concentration for both Tigris and Euphrates for the tap water was found in **Al- Sulaimaniyah**, and the highest level of chloride concentration of tap water was found in **Al- Diwaniyah**, for river water the lowest chloride concentration was found in **Al- Mosul** and the highest level of chloride concentration in river water was also found in **Al- Diwaniyah**. In **Baghdad** the chloride concentration in the ground water was found to be lower than its concentration in the river and tap water. The same results were obtained for **Al- Sulaimaniyah** ground water sample.

The governorates lie at Tigris, the concentration of chloride in tap was higher than its concentration in the river water, but for the governorates lies at Euphrates, the concentration in the tap water was lower than its concentration in river water.

Governorates lie at Tigris, the tap and river water chloride concentration increases from the north down to the south of the river direction except in **Baghdad (Qadissyah Q.)** which was lower than chloride in **Diyala** for both tap and river water. The same was found in governorates which lie at Euphrates in which the chloride concentration increases from north down to the south of the river direction. However, the chloride concentration in tap and river water of the governorates lie at the Tigris river was found to be lower than the chloride concentration for the governorates which lie at Euphrates river. The chloride distribution in water samples measured by this method were shown in figure (3-17)

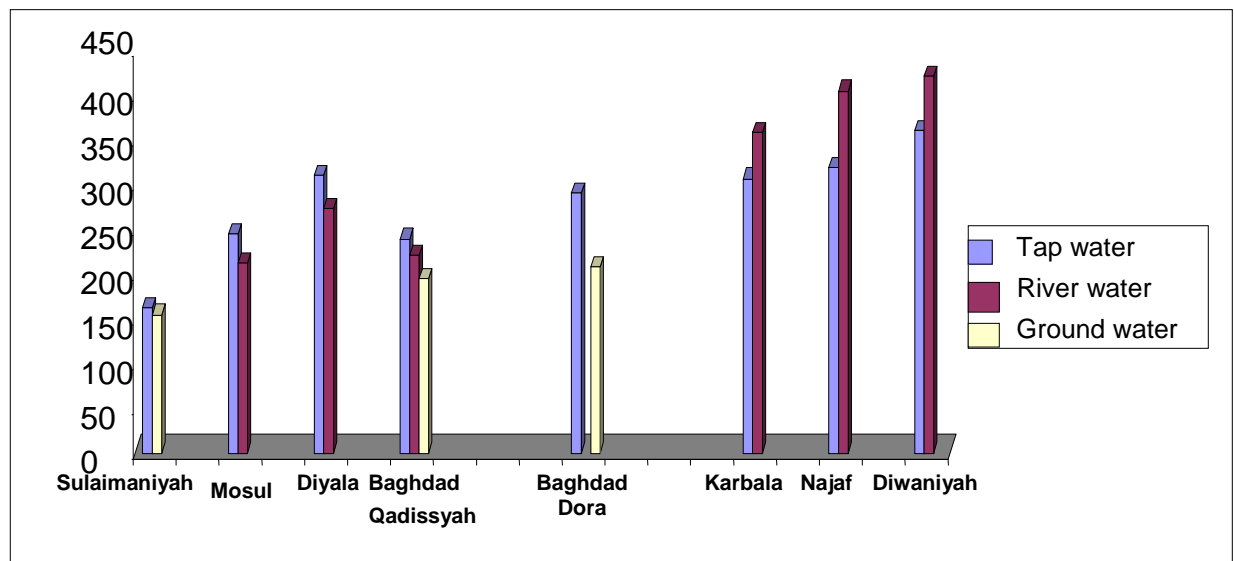


Fig (3-17) Chloride distribution in tap, river and ground water measured by the titration

The recovery and error were measured for chloride standards by titration with silver nitrate are shown in the table (3-12).

Table (3-12) Recovery and relative error for chloride standards measured by the titration with silver nitrate

parameters	chloride
Concentration prepared (M)	1×10^{-3}
Found (M)	0.9598×10^{-3}
Recovery %	95.98
Relative Error %	4.02

The recovery of chloride which obtained from the measuring by the titration was lower than the recovery of chloride which obtained by ion selective electrode 99.31.

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 as shown in the table (3-13).

Table (3-13) Concentration of ions in ground water

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

All metal ions concentration in the river water samples were found to be the highest in **Al- Diwaniyah**, while the lower concentration were found in **Al- Mosul** as shown in the table (3-14)

Table (3-14) Concentration of ions in river water

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

*Not found

Lead was not found in all these samples. The metal ions concentrations were found to increased 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 (3-15) 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 (3-15) Concentration of ions in tap water

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

* 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 ^[89]. 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 ^[89]. 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 ^[89].

The acidity and temperature of water can also increase the rate of pipes corrosion to a significant degree ^[91].

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 (1-1) and (1-2) in chapter one. 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 (1-1).

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 determinations 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 (3-16) for comparison.

Table (3-16) Metal ions concentration measured by ISE, AAS and the titration

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

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

Conclusion

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.

Future work

- 1- Determination of other metal ions in water such as sulfide, phosphate, mercury, manganese, chromium, sodium and potassium and others, also determine the biological oxygen domain (BOD) in all water samples.
- 2- Study of water quality by collecting other water samples from other Iraqi water resources, and collecting samples before and after the water treatment plants.

2. Experimental part

2.1 Instruments and equipments

Jenway ion meter, model 3345, with single and double junction reference electrodes, (England).

Calcium and chloride ion selective electrodes obtained from Orion research incorporated, (Boston, USA), cupric combination selective electrode, jenway, (924-393).

PERKIN-ELMER Flame atomic absorption spectrophotometer, model 5000 (USA). Ca, Cu, Fe, Mg and Pb hollow cathode lamps were obtained from PERKIN-ELMER instruments.

2.2 Chemicals

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

2.3 Sampling

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.

2.4 preparations of standard solutions

All solutions were prepared in doubly distilled deionized water (resistivity $\sim 18 \text{ M}\Omega$).

2.4.1 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 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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.

2.4.1.1 Calibration of the ISEs

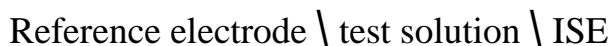
The electrode has been calibrated by measuring a series of known standard solutions, made by serial dilution of the 1000 ppm stock solutions for full calibration.

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

2.4.1.2 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:



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.

2.4.1.3 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

2.4.2 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, 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.

2.4.2.1 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.

2.4.3 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 ^[87].

List of content

Summary		<i>I</i>
List of contents		<i>III</i>
List of figures		<i>VI</i>
List of tables		<i>VIII</i>
Abbreviations		<i>x</i>
Contents of chapter one		
1-1	Water resources	1
1.1.1	Water quality	1
1.1.2	Water pollutants	2
1.1.2.1	Some of elements exist in water	3
	• Copper	3
	• Lead	3
	• Iron	4
	• Calcium	4
	• Magnesium	5
	• Chloride	5
1.1.3	Origin and source of water pollution	7
1.1.3.1	Origin and sources of water pollutants	7
1.1.3.1a	Natural source of run off	8
1.1.3.1b	Domestic sewage	8
1.1.3.1c	Agriculture wastes	9
1.1.3.1d	Industrial wastes	10

1.2	Electrochemical techniques	10
1.2.1	Electrochemical cell	11
1.2.2	Ion selective electrode	12
1.2.2.1	General applications of ISEs	14
1.2.2.2	Potentiometric measurements	15
1.2.2.3	Ions analyses using ISEs	16
1.3	Atomic absorption spectroscopy	17
1.3.1	General applications of AAS	17
1.3.2	Metals analyses by AAS	18
1.4	Aim of the work	20
Contents of Chapter two		
2.1	Instruments and equipments	21
2.2	Chemicals	21
2.3	Sampling	21
2.4	Preparation of standard solutions	22
2.4.1	Preparation of standard solutions for ISEs measurements	22
	• Calcium	22
	• Copper	22
	• Chloride	22
2.4.1.1	Calibration of ISE measurements	22
2.4.1.2	Potentiometric measurements	22
2.4.1.3	Samples analysis	23
2.4.2	Preparation of standard solutions for AAS measurements	23

	<ul style="list-style-type: none"> • Calcium • Copper • Lead • Iron • Magnesium 	23 24 24 24 24
2.4.2.1	Calibration for AAS measurements	24
2.4.3	Determination of chloride	25
Contents of chapter three		
3.1	Quantitative analysis by ISEs <ul style="list-style-type: none"> • Calcium • Copper • Chloride 	26 26 29 32
3.2	Quantitative analysis by AAS <ul style="list-style-type: none"> • Iron • Lead • Copper • Magnesium • Calcium 	36 36 39 42 45 48
3.3	Quantitative chloride determination by titration	52
Conclusion		60
Future work		61
References		62

List of figures

1-1	The distribution of domestic sewage components	9
3-1	Calibration of calcium ion selective electrode	26
3-2	Calcium distribution in tap, river and ground water measured by ion selective electrode	29
3-3	Calibration of cupric ion selective electrode	29
3-4	Copper distribution in tap, river and ground water measured by ion selective electrode	32
3-5	Calibration of chloride ion selective electrode	32
3-6	Chloride distribution in tap, river and ground water measured by ion selective electrode	35
3-7	Calibration curve of iron	36
3-8	Iron distribution in tap, river and ground water measured by atomic absorption	38
3-9	Calibration curve of lead	39
3-10	Lead distribution in tap water measured by atomic absorption	41
3-11	Calibration curve of copper in AAS	42
3-12	Copper distribution in tap, river and ground water measured by atomic absorption.	44

3-13	Calibration curve of magnesium	45
3-14	Magnesium distribution in tap, river and ground water measured by atomic absorption.	47
3-15	Calibration curve of calcium in AAS	48
3-16	Calcium distribution in tap, river and ground water measured by atomic absorption.	50
3-17	Chloride distribution in tap, river and ground water measured by the titration	54

List of tables

1-1	The maximum contamination level of elements in drinking water	6
1-2	The maximum level of elements in drinking water according to (C.O.S.Q.C)	7
1-3	Some ion selective electrode and their characterization and parameters.	13
3-1	Calcium concentration determined by ion selective electrode in different water samples in Iraq	27
3-2	Copper concentration determined by cupric ion selective electrode in different water samples in Iraq	30
3-3	Chloride concentration determined by chloride ion selective electrode in different water samples in Iraq	33
3-4	Recovery of the ions which measured by ion selective electrode	35
3-5	Iron concentration determined by atomic absorption in different water samples in Iraq	37

3-6	Lead concentration determined by atomic absorption in different water samples in Iraq	40
3-7	Copper concentration determined by atomic absorption in different water samples in Iraq	43
3-8	Magnesium concentration in different water samples in Iraq	46
3-9	Calcium concentration determined by atomic absorption in different water samples in Iraq	49
3-10	Recovery and error for standard of metals measured by AAS	51
3-11	Chloride concentration determined by titration with AgNO_3 in different water samples in Iraq	52
3-12	Recovery and error for chloride standards measured by the titration with silver nitrate	54
3-13	Concentrations of ions in ground water	55

3-14	Concentrations of ions in river water	55
3-15	Concentrations of ions in tap water	56
3-16	Metal ions concentration measured by ISE, AAS and titration	59

Abbreviations

AAS	Atomic absorption spectroscopy
ISE	Ion selective electrode
TW	Tap water
RW	River water
GW	Ground water
SD	Standard deviation
RSD	Relative standard deviation
EPA	Environmental protection agency
EEC	European economic commodity for environmental legislation
WHO	World health organization
ppm	Part per million
ISA	Ionic strength adjuster

الاسم: **حازم محمد الرزاق محمد الامير محباس الزبيدي**

التحصيل الدراسي: **خريج بكالوريوس (٢٠٠٣) و ماجستير (٢٠٠٦)**

من جامعة النهرين/ كلية العلوم/ قسم الكيمياء/ الاختصاص (كيمياء

تحليلية)

اسم الاطروحة: **(نوعية المياه في بعض مصادر المياه العراقيه)**

(Water Quality in Some Iraqi Water Resources)

موعد المناقشه: **٢٠٠٦/٧/٢٧**

العنوان: **بغداد حي القادسيه محله/٤٠٤ زقاق/٢٥ رقم الدار/٦/١**

رقم الهاتف: **٠٧٩٠١٢٩٣٤٥٥**

References

- 1- Goel, P.K., "Water pollution causes, effect and control", published by new age international, New Delhi, (1997).
- 2- Governor Bob Tafi; Speck Samuel W.; Dick bartz, "Ground Water Quality", Ohio department of natural resources division of water, (1987).
- 3- Atilas Jorge H., "Testing For Water Quality", the University of Georgia, (2003).
- 4- "Research in Analytical Environmental Trace Elements Chemistry and Its Impact on Water Quality", National Research Program (NRP), US Geological Survey, (1996).
- 5- Hanson Lyle K. "2001 Water Quality Report", Cader Rapids Water Department, (2001).
- 6- Shin Suke Ohio, Miho Tanaka, "Successive determination of copper and iron by a flow injection catalytic photometric method a serial flow cell", Analytical Science, **20**, 171, (2003).
- 7- Lee Samuel S. "Copper in industrial waste water and its removal"
- 8- Cathy Burwell, "Lead in Drinking Water", Department of consumer science and relating, (1991).
- 9- Mary Tiemann, "Lead in Drinking Water; Washington DC, issues and broader regulatory implications", congressional research service, the library of congress, Washington DC, (2005).
- 10- "Iron In Drinking Water", Bureau of drinking water & ground water, Wisconsin Department of Natural Resource, Washington DC, (2001).
- 11- Batto, R. I., spectrochem. Acta Rew, **14**, 141, 1991.
- 12- Forst new vittman, "Metal pollution in the aquatic environment", New York, 17, 1979.

References

- 13- Drilla L.; Hale T., J. Am. Collimator Nutr, **11 (3)**, 326-329, (1992).
- 14- Day, E.H., "The chemical elements in nature", George C. Harrap & Co., London, UK, (1963).
- 15- "Drinking water monitoring data", Ontario Ministry of Environment, (1987).
- 16- Rocker, R.R.; Heaney, R.P., "The effect of milk supplements on calcium metabolism, bone metabolism and calcium balance", Am. J. Clin. Nutr, **41**, 254, (1985).
- 17- "Metals in drinking water", visit at <http://WWW.metals in drinking water AG. 473-1-htm>.
- 18- Y. Yamamoto, 4. Yamazki, and T. Sakurai J. Anal Chem., Sec. **104**, 2329-2330, (1982).
- 19- "Health Criteria and other supporting information", World health organization Geneva, **2**, 248-253, (1996).
- 20- P.G., Angali; V.R., Marrathi, Inorg. Chem., **14**, 970-973, (1975).
- 21- "Aqua pure water filters", visit at <WWW.aqua pure filters.com/contamination/118/chloride.html>.
- 22- "Guidelines for drinking water quality", WHO guidelines for drinking water quality, world health organization, Geneva, (2003).
- 23- "Drinking water quidelines", visit at <www.hach.com>
- 24- "Drinking water", Iraqi central organization for standardization and quality control, standard specification No. 417, (2001).
- 25- Bauer Henry H.; Christian Gary D.; O'rielly James E., "Instrumental analysis", Allya and Bacon, Inc., Boston, (1985).
- 26- Ewing Galen W., "Instrumental methods of chemical analysis", Fifth edition, McGraw-Hill BOOK Co., New York, (1985).
- 27- Anderson Mark R., "Potentiometry", also visit at www.chem.vt.edu/chem-ed, (2000).

References

- 28- Sawyer Donald T.; Heineman William R.; Beebe Janice M., "Chemistry experiments for instrumental methods", John Wiley & Sons Inc. (1984).
- 29- Hillarad Hobart H.; Merritt Lynne L.; Dean John A., "Instrumental methods of analysis", fourth edition, (1965).
- 30- Lynde Stuart R., "Environmental sampling and monitoring primer", (2002).
- 31- Douglas A. Skoage, "Principle of instrumental analysis", Third edition, Saunders collage publishing, Florida, (1985).
- 32- Koryta, J., Ed., "Medical and Biological applications of electrochemical devise", Wiley, Chichesrer, (1980).
- 33- Baily, P.L., "Analysis with ion selective electrode", second edition, Heyden, London, (1980).
- 34- Koryta, J., "Ion selective electrode", Cambridge university press, Cambridge, England, (1974).
- 35- Steven, G.D.; Richard, G.C.; John, E; Lynn, F.G., Oxford chemistry primers, Oxford university press, 4,(1999).
- 36- Parathasarathy, N.; Buff, J. and Monnier, D.; Anal. Chim. Acta. 68, 185, (1974).
- 37- Buff, J., Parathasarathy, N.; and Haerdi, W., Anal. Chim. Acta, 68, 253, (1974).
- 38- Aberlin, M.E.; and Bunton, C.A.; J. Org. Chem., 35, 1825, (1970).
- 39- Knovel, A.M. and Kehr, P.F.; Anal. Chem., 44, 1865 (1972).
- 40- Milham, P.J.; Awad, A.S.; Paull, R.E. and Bull, J.H.; Analyst, 95, 751, (1970).
- 41- Ingram, B.L.; Anal. Chem., 42, 1825, (1970).
- 42- Hipp, B.W. and Langdal, G.W.; Soilsa. Plant Anal., 2, 237, (1971).
- 43- Hallam, A.I.; Pilts, G.; and Hollis, J.P.; Soil Sci., 114, 456 (1972).

References

- 44-Goertzen, J.D. and Oster J.D.; Soil. Sci. Soc., **116**, 311, (1974).
- 45- Cheng, K.L.; Hung, J.C. and Prager, D.H.; J. Microchem., **18**, 256, (1973).
- 46- Bremmer, J.M., and Tabatabai, H.M.; Commum. Soil. Sci. Plant Anal., **3**, 159, (1972).
- 47- Morie, G.P.; Ledford, G.J. and Glover, C.A.; Anal. Chim., Acta, **60**, 397, (1972).
- 48- Harries, R.C. and Williams, H.H.; J. Appl. Metrol., **8**, 299, (1969).
- 49- Torrance, K.; Analyst, **99**, 203 (1974).
- 50- Mellon, E.F. and Gruber, H.A.; J. Am. Leather Chem., **65**, 154, (1970).
- 51- Lawes , B.C.; Fournier, L.B. and Mthere, O.B., Plating, **60**, 902, (1973).
- 52- Heistand, R.N. and Blak, C.T.; Mikrochem. Acta., **212**, (1972).
- 53- Ridden, J.M.C.; Barefoot, R.R. and Roy, J.G.; Anal. Chem., **43**, 1109, (1971).
- 54- Baumann, E.W.; Anal. Chem., **42**, 110, (1970).
- 55- Overman, R.F.; Anal. Chem., **43**, 616, (1971).
- 56- Rodrinquez, H.J.; Villarreal, H.; Klaper, S. and Slatopolstky, E.; J. Clin. Endocrinol. Metab., **39**, 693, (1974).
- 57- Fuchs, J.C. and Desmet, G.; G. Clin, Chim. Acta, **47**, 357, (1973).
- 58- Lustgarten, J.A.; Wenk, R.B.; Byrd, C. and Hall , B.; J. Clin. Chem., **20**, 1217, (1974).
- 59- Smith, M.D.; Rogers, R.W.; Genshow, M.A. and Greyson; J. Clin. Chem., **19**, 891, (1973).
- 60- Person, T.J., and Gray, C.M.; J. Hosp. Pharm., **31**, 20, (1973).
- 61- Wise, W.M.; Kurey, M.J., and Baum, C.; J. Clin., Chem., **16**, 103, (1970).

References

- 62- "Introduction to ion selective electrodes advantages", visit at WWW.nico2000.net/index.html., (2002).
- 63- Baily, P.L., "Analysis with ion selective electrodes", Heyden and Son Ltd., (1976).
- 64- Durst, R.D., In ion selective electrodes, Durst R.D. editor, Chapter 114, N.B.S. spc. Publ. No. 314, Washington, DC.,(1969).
- 65- Gavagnaro, D.M., US. Nat. Tech. Inform. Serv., RS Report No.791, 1025, Avail. NTIS, 177 PP, (1979).
- 66- Vanderlinden, W.E.; Oostervink, R., Anal. Chim. Acta., **101**, 4199-22, (1978).
- 67- Stella, R.; Ganzerli-valentini, M.T., Anal. Chem., **51**, 2148-51.
- 68- Westall, J.C.; Morel, F.M.M and Hume, D.N., Anal. Chem., **51**, 1792-8, (1979).
- 69- "Water quality determination of chloride", International organization for standardization, Geneva, (1989).
- 70- "Methodss for the examination of waters and associated materials; chloride in waters, sewage and effluents", department of environment, London, Her majesty's stationary office, (1981).
- 71- "Direct potentiometric determination of calcium in waters with a constant complexation buffer", Hulanick, A.; Trojanowica, M., Anal. Chim. Acta, **68**, 155, (1974).
- 72- Kawamura, M. and Kashimu, T., Jap. Analyst, **16**, (1971).
- 73- Hu, Z.; Hu, W. and Qi, D., Fenxi Huaxue, **14 (21)**, 1460, (1991).
- 74- Grossmann, H.; Mortiz,W.; Szeponik, J.; Borchert, C., Z. Wasser Abwasser For Sch., **24**, 76-80, (1991).
- 75- Ingie James D.,JR., "Spectrochemical analysis", Prentice-Hall international, Inc. USA, (1988).
- 76- Sturgeon, R.E.; Bwrman, S.S.; Desaulniers, A. and Russel, D.S., Anal. Chem. Abstr., **93**, 31507v, (1980).

References

- 77- Coxim, Campbell M.J. and Dowson D., *Lancet*, **337**, 757-760, (1991).
- 78- "Environmental Health Perspectives", **109**, No.3, (2001).
- 79- Fishman, M.J. and Downs, S.C., "Methods for analysis of selected metals in water by atomic absorption", Geological survey, water supply paper, US.government printing office, Washington, DC., (1966).
- 80- "Standard methods for the examination of water and waste water", 17th edition, American public health Association, Washington, DC., (1989).
- 81- Dawson, J.B. and Heaton, F.W., "The determination of magnesium in biological materials by atomic absorption spectrophotometry", department of medical physics, Leeds, (1960).
- 82- Gautam Samenta and D. Chakrabort, J., *Anal. Chem.*, **357**, issue 7, 87-832, (1997).
- 83- Taher Mohammad Ali, "Flame atomic absorption spectrometric determination of trace lead after solid liquid extraction and preconcentration using 1-(2-pyridylazo)-2-naphthol", department of chemistry, shahid Bahonar university, Kerman, Iran, (2003).
- 84- Ranweiler, L.E. and J.L. Mogres, *Eniro. Sic. Techno.*, **8**,152, (1974).
- 85- Gibert, T.R. and D.N. Hume, *Anal. Chem. Acta*, **65**,451, (1973).
- 86- Thomas, R. Gilbert, *Anal. Chem. Acta.*, **65**, 451, (1973).
- 87- Arthur I. Vogel, *Textbook of "quantitative inorganic analysis"*, third edition, London, (1961).
- 88- Sienko, M.J. and Plane, R.A., "Chemical principles and properties", second edition, McGraw-Hall, New York, (1974).
- 89- "Bechtel's Dry Run Iraqis suffer water crisis", also visit at www.wateractivist.org, April (2004).

References

90- Paul, F. Vendrell and Jorge. H. Atilas," Corrosive or Scaling water", the University of Georgia, (2003).

91- "Home water quality and safety", university of Florida, (1986).

Summary

This study represents a small contribution to draw attention towards the water quality with respect to the amount of the metal ions (calcium, magnesium, chloride, copper, iron and lead) in some Iraqi water resources (tap, river and ground water). The water samples was collected from some Iraqi governorates (Al- Sulaimaniyah, Al- Mosul, Diyala, Baghdad, Karbala, Al- Najaf, and Al- Diwaniyah).

In chapter one of this thesis, an introduction was given on the water resources and water quality also the water pollutants and their origin and sources, and some metal ions that may exist in the drinking water and their maximum level according to the Iraqi and international water quality standards. Chapter one also concerns with the analytical techniques used to determine the metal ions in water samples. These methods include the electrochemical and spectrochemical techniques.

The second chapter deals with experimental part, which include instruments, chemicals and sampling. Chapter two also describes the methods used to determine metal ions in the water samples.

The results and discussion was presented in chapter three. The results included the determination of Ca^{++} , Mg^{++} , Cl^- , Cu^{++} , Fe, and finely Pb ion concentrations.

The calcium concentration in water samples were in the range (20.73 to 44.66) ppm in tap water, (39.19 to 73.19) ppm in river water and (32.42 to 58.79) ppm in ground water.

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 in water samples 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 in the tap water, (18.53 to 33.33) ppm in the river water and (15.53 to 23.09) ppm in the ground water samples.

Iron concentration was in the range (0.135 to 0.273) ppm in the tap water, (0.127 to 0.221) ppm in the river water and (0.078 to 0.095) ppm in the ground water samples.

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.

الخلاصة

تمثل هذه الدراسة أسهاماً صغيراً تهدف إلى تعيين تراكيز بعض الأيونات (الكالسيوم و المغنيسيوم و الكلورايد و النحاس و الحديد و الرصاص)، في بعض مصادر المياه (ماء الشرب، ماء النهر و ماء البئر). جمعت عينات الماء جمعت من بعض محافظات العراق (السليمانية، الموصل، ديالى، بغداد، كربلاء، النجف و الديوانية).

الفصل الأول في هذه الأطروحة هو المقدمة و التي احتوت على كل من مصادر المياه و نوعيه المياه و ملوثات المياه و اصلها و مصادرها ثم بعض المواد التي يمكن ان توجد في ماء الشرب و الحد الاعلى المسموح به لوجود تراكيزها في ماء الشرب حسب المواصفات العراقية و بعض المواصفات العالميه.

كما احتوى الفصل الاول على بعض التقنيات و الطرق التحليلية لقياس تراكيز المواد الموجوده في الماء، و هذه الطرق تشمل بعض التقنيات الكهروكيميائية و التقنيات الطيفية.

الفصل الثاني يتعامل مع الجزء العملي، و الذي يتضمن الاجهزه و المواد الكيميائية المستخدمه و كذلك جمع العينات، الفصل الثاني ايضا احتوى على طرق قياس الايونات في عينات المياه.

النتائج و المناقشه عرضت في الفصل الثالث، النتائج تضمنت تعيين تراكيز الايونات (الكالسيوم و المغنيسيوم و الكلورايد و النحاس و الحديد و الرصاص) في بعض مصادر المياه العراقية المذكوره سابقا.

بالنسبه لعينات ماء الشرب كان تركيز الكالسيوم يتراوح بين (٢٠,٧٣ الى ٤٤,٦٦) ملغم/لتر، و لماء النهر كان (٣٩,١٩ الى ٧٣,١٩) ملغم/لتر، اما بالنسبه لعينات ماء البئر فكان تركيز الكالسيوم يتراوح بين (٣٢,٤٢ الى ٥٨,٧٩) ملغم/لتر.

كان تركيز النحاس يتراوح بين (٠,٠٥٣ الى ٠,١٠٥)، (٠,٠٣٦ الى ٠,٠٦٩) و (٠,٠٣٥ الى ٠,٠٥٨) ملغم/لتر في ماء الشرب، النهر و عينات ماء البئر بالتوالي.

كان تركيز الكلورايد يتراوح بين (١٦٧,٠٤ الى ٣٧٠,٠١)، (٢١٦,٨١ الى ٤٣٣,٧٥) و (١٤٨,٦١ الى ٢٠٩,٤٥) ملغم/لتر في ماء الشرب، النهر و عينات ماء البئر بالتوالي. كان كان

تركيز المغنيسيوم في عينات المياه يتراوح بين (٧,٨٧ الى ١٨,٩١) ملغم/لتر في ماء الشرب و (٣٣,٣٣ الى ١٨,٥٣) ملغم/لتر في ماء النهر و (٢٣,٠٩ الى ١٥,٥٣) ملغم/لتر في عينات

ماء البئر.

كان تركيز الحديد في عينات المياه يتراوح بين (٠,١٣٥ الى ٠,٢٧٣) ملغم/لتر في ماء الشرب و (٠,١٢٧ الى ٠,٢٢١) ملغم/لتر في ماء النهر و (٠,٠٧٨ الى ٠,٠٩٥) ملغم/لتر في عينات ماء البئر.

اما تركيز الرصاص في عينات مياه الشرب كان يتراوح بين (٠,٠٠٨ الى ٠,٠١٣) ملغم/لتر و لم يوجد تركيز للرصاص لا في عينات مياه النهر ولا في عينات مياه البئر في هذه الدراسة.

Republic of Iraq
Ministry of Higher Education and Scientific Research
Al-Nahrain University
College of Science
Department of Chemistry



Water Quality in Some Iraqi Water Resources

A Thesis Submitted to the College of Science Al-Nahrain University in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry

By
Hazim Abdul Razzaq Abdul Ameir
(B.Sc 2003)

July 2006

1427

Supervisor certification

I certify that this thesis was prepared under my supervision at the Department of Chemistry, College of Science, Al-Nahrain University as partial requirements for the Degree of Master of Science in Chemistry.

Assistant Professor

Dr. Shahbaz A. Maki

In view of the available recommendation, I forward this thesis for debate by the Examining Committee.

Assistant Professor

Dr. Afaf Al-Derzi

Head of the Department
of Chemistry College of
Science Al-Nahrain
University

Examining Committee's Certification

We, the Examining Committee, certify that we read this thesis and have examined the student **Hazim Abdul Razzaq**, in its contents and that, in our opinion; it is adequate as a thesis for the Degree of Master of Science, in Chemistry.

Signature:

Name:
(Chairman).

Signature:

Name:
(Member)

Signature:

Name:
(Member)

Signature:

Name: Dr. Shahbaz A. Maki
(Member\advisor)

Approved for the College of Graduate Studies

Assistant Professor

Dr. Laith ABD AL- AZIZ AL ANI

Dean of College of Science Al-Nahrain University

بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ

وَجَعَلْنَا مِنَ الْمَاءِ كُلَّ

شَيْءٍ حَيًّا

صَدَقَ اللّٰهُ الْعَظِیْمُ

سورة الأنبياء

الآية ٣٠

الأهداء

الى الغالي الذي ما زالت روحه تلازمني

و تنير لي حياتي

اخي الغالي انهار

الى الذين أحبوا و تمنوا لي النجاح

الى الذين صبروا و تحملوا لأجل ذلك الكثير

أعز الناس

والدتي و والدي

الى من اشد بهم ازري في الحياة

أخي و اختي

الى أولاد اخي الملائكة الصغار

يوسف و ساره

الى رفاق الدرب الطويل

أصدقائي

اهدي هذا الجهد المتواضع

حازم

ACKNOWLEDGEMENT

Praise be to Allah the Lord of the worlds and peace and blessings be upon the master of humankind Muhammad and his pure Progency and his relatives and may God curse their enemies until the Day of Judgment.

I would like to express my deepest thanks to my respected Supervisors Dr. Shahbaz A. Maki for his great help and assistance provided during this work,

I am especially grateful to my friend Ahmed and Salwan and Mohammad R. and Mohammad H. and Sarmad for there help in justifying this thesis.

Sincere thanks are also to the Dean of the college of science and the head of department of chemistry and the staff member of the department of chemistry.

Finally to all my friends..... I present my thanks.

Hazzim

2006



جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين/كلية العلوم
قسم الكيمياء

نوعية المياه في بعض مصادر المياه العراقية

رسالة
مقدمة إلى كلية العلوم - جامعة النهرين
وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل

حازم عبد الرزاق عبد الأمير

بكالوريوس ٢٠٠٣ (جامعة النهرين)

تموز ٢٠٠٦

١٤٢٧