University of Benghazi
Faculty of Science
Department of Chemistry

Estimation of Lead And Cadmium in Benghazi city coast using Atomic Absorption Spectroscopy

M. Sc. Thesis
By:
Mohammed Younis Mohammed

Supervised by
Dr. Satea S. El Atrash

Thesis submitted in partial fulfillment of the requirements of the Degree of Master of Science in Chemistry
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Abstract:

Seawater is a complex solution containing, either a dissolved or particulate, all of the elements of the earth's crust. Have been affecting human and living things in the various fields.

Therefore, much interest and effort have been devoted on the studies for the determination of these elements. These elements are presented at lower level than the detection limits of common analytical methods, and their determination is spectroscopically and chemically interfered with other major constituents. Much effort has been tried to solve difficulties of such interferences by the development of various techniques. In order to eliminate the interferences, a solvent extraction has been commonly applied for the separative concentration of trace elements from the sample matrix. Dithizone and its derivatives and oxine are used for such extraction.

This technique has advantages of relatively easy experimental procedure and good selectivity as well as a disadvantage of low concentration efficiency. That is, some auxiliary ligands have been used together with a main ligand. Such as, KCN and KSCN.

In this research, we measured the trace amounts of lead and cadmium after preconcentration of the samples from the coast of Benghazi.

The preconcentration of trace amounts of lead and cadmium for using Flame Atomic Absorption Spectrometer by a solvent extraction Dithizone complex was formed at pH 7-9 for removed interferences.

The maximum extraction time was found to be 30 minutes, the lead-Dithizone complex shows maximum absorbance at 283.3nm; and the Cadmium-Dithizone complex shows maximum absorbance at 228.8 nm.

1.1. General introduction of Lead:

Lead is a member of subgroup **IVA** of the periodic table, it is a typical heavy metal **(**Lippmann, 2000**)**, with atomic number 82 and mass number 207.21a.m.u (Weiss, 1972, House et al, 2005), ground state electronic configuration is [Xe]$6s^{2}4f^{14}5d^{10}6p^{2}$.
It has a relatively high mass number. The chemical symbol **Pb** is for ***Plumbum,*** the latin word to denote spouts or water conductors, with its modern counterpart in our word plumber (Weiss, 1972). The elements in group **IVA** Carbon, Silicon, Germanium, Tin and Lead-shown a graduation from C, which is non-metallic to Pb, which though its oxides are amphoteric, is mainly metallic in nature (House et al, 2005). Valence shell of the lead atom it's outer shell. Lead has no allotropic modification and crystallizes with face-centered cubic structure (a = 4.9489A°), with nearest neighbor Lead-Lead distance as 3.49 A° (H. P. Klug, 1946).

Lead, together with Iridium and Thallium, form a group of close-packed metals isolated from the other close-packed metals, the inter-atom distances in Iridium, Thallium and Lead are very large compared with those of neighboring elements (A. F. Wells, 1962).

The element would be expected to show a normal valence +4 in its compound, the two **s** electrons of lead are reluctant to ionize and are thus sometimes referred to as the inert pair, all members of group **IVA** exhibit an oxidation state of +4, but the +2 oxidation state increases in stability as the group is descended. Lead is considered to have a stable oxidation state (Pb^{2+}) that furnishes a divalent ion (Lippmann, 2000 , House, 2005).
In the earth's crust lead is estimated to be present as 1.6×10^{-3} % by weight and to be in seawater at a concentration of 4 ppb (Rochow et al,1973).

1.2. lead in the environment:

Lead exist in a large number of minerals, and is associated with other metals, notable zinc and silver, and to a lesser extent copper and gold, the occurrence of lead in its native state is rare (Weiss et al, 1972).

The most important lead ore is galena PbS, which is widely distributed throughout the world (Rochow et al, 1973, Clark, 2001), it is frequently associated with sphalerite (ZnS), pyrite FeS_2 and marc site white iron pyrite, of lesser commercial importance are cerussite $PbCO_3$, anglesite $PbSO_4$, pyromorphite $PbCl_2.3Pb_3(PO_4)_2$ (Weiss et al, 1972, Rochow et al, 1973) and Mimetesite $PbCl_2.3Pb_3(AsO_4)_2$ (Rochow et al, 1973).

Another lesser minerals are crocoites (or kallochrome, or red-lead ore) ($PbCrO_4$), wulfenite (or molybdenum lead spar, or yellow lead ore) ($PbMoO_4$) and stolzite ($PbWO_4$) (Rochow et al, 1973), Lead is also found in Silicates, Vanadates, Arsenates, and other minerals (Weiss et al, 1972).

On the second hand, the implementation of stricter environmental policies has already shown that the Mediterranean environment is very sensitive to changes in emissions of anthropogenic TMs. For example, the implementation of the antipollution policy on automotive lead in the second half of the 1980s has resulted in the rapid removal of lead in the North-western Mediterranean atmosphere (Migon et al, 2008).

Briefly, tetra-ethyl Pb was used until the 1990s as an additive in gasoline to increase its octane rating (Kummer et al., 2009).

1.3. Properties of lead:

Lead (Pb) in its elemental form is silvery-white and turns blue-grey when exposed to air. The outstanding physical properties of pure lead are its high density, softness, malleability, flexibility, low melting point, low strength and low elastic limit, these characteristics together with its high corrosion resistance (Weiss et al, 1972, House et al, 2005), are the basis of most applications of lead metal, also high expansion coefficient. Lead is diamagnetic, poor conductor of electricity and exhibits high damping characteristics for mechanical and acoustical vibration.

A high mass absorption coefficient makes lead very effective in attenuating X-rays and gamma rays (Weiss et al, 1972). Pure lead is bluish-white in color and has a bright luster (Weiss et al, 1972, Rochow et al, 1973), with air and water vapor the metal forms a thin surface film of oxycarbonate which protects the underlying metal.

physical properties of Lead:

Atomic number-82, Atomic mass-207.2 g.mol^{-1}, Electronegativity according to Pauling-1.8, Density-11.34 g.cm^{-3} at 20°C, Melting point-327 °C, Boiling point-1755 °C, Vanderwaals radius-0.154 nm, Electronic shell-[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^2$, Isotopes-13, Ionic radius-0.132 nm (2+) ; 0.084 nm (4+), Energy of first ionization-715.4 kJ.mol^{-1}, Energy of second ionization-1450.0 kJ.mol^{-1}, Energy of third ionization-3080.7 kJ.mol^{-1}, Energy of fourth ionization-4082.3 kJ.mol^{-1}, Energy of fifth ionization-6608 kJ.mol^{-1} and Discovered by-The ancients (Thurmer et al, 2002, UNEP, 2008).

1.4. Industrial and commercial utilization of lead:

The current annual worldwide production of lead is approximately 5.4 million tons and continues but because lead is easily refined, and does not normally become contaminated in service, lead and lead-alloy scrap constitutes an important factor in re-enters the market.

The following list gives an approximate indication of some of the major consumers of lead; Storage batteries (~35%) (Weiss et al, 1972, Rochow et al, 1973), tetraethyl lead (~10%), cable covering (~10%) (Weiss et al, 1972, Rochow et al, 1973), solder (~10%), red lead and litharge (~5%), building lead (~5%) and caulking (~5%) (Rochow et al, 1973).

Lead is soft metal and has been widely used in the plumbing industry except in isolated cases, lead is probably not a major problem in drinking water, although the potential exist cases where old lead pipe is still in use.

Water that has stood in household plumbing for some time may accumulate significant levels of lead (along with zinc, cadmium and copper) and should be drained for a while before use. Lead oxide are of great commercial importance, e.g. in the manufacture of "crystal lead" glass. Read lead Pb_3O_4 is used as a pigment and a corrosion-resistant coating for steel and iron (House, 2005).

The use of lead increased during the medieval ages as a roofing material, for war projections of lead include plumbing material and containers for corrosive liquid such as sulfuric acid (Weiss et al, 1972).

Since leaded gasoline was introduced in 1923, its combustion and resulting contamination of the atmosphere. One source of environmental lead, tetraethyl lead, was to be reduced in the UK from 0.4 to 0.15 g/l in petrol by the end of 1985.

Large quantities are consumed in the manufacture of tetraethyl lead, an antiknock compound in gasoline (Weiss et al, 1972), although worldwide phase-out of leaded gasoline is in progress, it is still being used all over the world.

Lead alloys with antimony, tin and other metals are used in making ammunition, solder, type metal and various antifriction metals (Weiss et al, 1972). Compounds of lead, such as white lead [$2PbCO_3.Pb(OH)_2$], sublimed white lead ($PbSO_4$), lead (Pb_3O_4), and chrome yellow ($PbCrO_4$) are used in paint.

The principal sources of environmental contamination of foods by lead are exhaust gases, industrial discharge and its presence in soil, industrial food processing can also give rise to lead contamination.

Lead is mined throughout the world, with major mining areas, yielding over 100,000 tons a year, in the U.S., Canada, Mexico, Peru, Yugoslavia, Australia, China, Bulgaria, and Some countries of the former Soviet Union.

In addition, between 800,000 to 1,000,000 tons are recovered from secondary or scrap sources annually.

In the U.S., over half a million tons of lead are produced from mine production, and a slightly larger amount from secondary lead (Weiss et al, 1972).

Lead pollution arises mainly from car exhausts but industrial processes, batteries, minerals and lead arsenate insecticide also contribute to lead in the environment (Timbrell, 2002).

1.5. Toxicity of lead:

Lead (II) ion interferes with a wide range of biochemical processes, it is probably the most dangerous ion of all. The general body of literature on lead toxicity indicates depending on the dose, lead exposure in children and adults can cause a wide spectrum of health problems, ranging from convulsions, coma, renal failure and death at the high end to subtly effects on metabolism and intelligence at the low end of exposures. Acute lead poisoning usually affects the gastro-intestinal trace or the nervous system, and occasionally it affects both (UNEP, 2008).

There can be a sweetish metallic taste, burning in the mouth, severe thirst, anorexia, nausea, severe headache and vomiting. Constipation is common, which may be interrupted by diarrhea due to gastroenteritis. Where all compounds of lead are toxic, and lead poisoning has been long known and exhaustively studied (Elkins, 1959), lead poisoning still constitutes one of the most important industrial hazards. Small quantities of lead are ingested regularly by humans from contaminated food and drink, but such quantities are easily eliminated by normal body processes.

Causes of harmful accumulations in this way are now very rare. Serious lead intoxication is now most frequently encountered by inhalation of vapors or dusts of lead and lead compounds, thus the processes of spraying or sanding lead paints are extremely hazardous without proper protection. The specified maximum allowable atmospheric pollution is 0.15mg of lead per cubic meter of air (Rochow, 1973).

Lead is a high toxic and cumulative poison, toxicity manifests as important of metabolic function, with possible change to the distribution and abundance of populations (Elder, 1988).

The toxicity of lead compounds depends on their solubility in body fluids, which may differ markedly from those in water, upon the particle size: when the particle is smaller, the solubility and toxicity are greater.

Blood lead concentrations provide probably the best index of recent exposure to this element and have been used for the biological monitoring of populations exposed to environmental lead in many countries (CED, 1977).

One considers that lead added to petrol is only one of many sources of lead, and possibly contributed only 20-30% of the total blood lead (Lead and Health,1980, Isotopic, 1982).

Lead, widely distributed as metallic lead, inorganic compounds and organometallic compounds, has a number of toxic effects, including inhibition of the synthesis of hemoglobin. It also adversely affects the central, peripheral nervous systems and the kidneys (Canham, 2000).

Lead is absorbed into the blood plasma, where it rapidly equilibrates with extracellular fluid, more slowly but within minutes, lead is transferred from plasma into blood cells (Lippmann, 2000), after absorption, lead enters the blood where 97 percent is taken up by the red blood cell, the half-life of lead in the red blood cell is 2-3 weeks, some redistribution of the lead to liver and kidney occurs and then excretion into the bile or deposition in bone takes place (Timbrell, 2002).

About 94-95% of the total body burden of lead is stored in the bones (Keating et al, 1987). This association with bone is related to the chemicals is similarity to calcium and the formation of insoluble lead phosphate (Lippmann, 2000).

Plant roots are usually able to take up and accumulate large quantities of Pb^{2+} in soil.

Found deposits of Pb, especially as pyrophosphate in the cell walls of the root but also similar deposits in stems, leaves and the occurrence of Pb granules may further explain the low toxicity (Pahlsson, 1989).

Individuals will absorb more lead in their food if their diets are deficient in calcium, iron or zinc (Mahaffey, 1990). Numerous studies have been conducted to determine the impact of this Pb burden on fish (Coughlan et al, 1986).

The measurement of trace metal concentration in marine organisms can be important in a wide range of applications, such as indicators of pollution (Goldberg et al, 1983, Prosi et al, 1981), studies of biochemical processes (Rainbow, 1985) and measurement of baseline levels (Fowler,1986, Martin et al, 1973).

Many marine crustaceans have been shown to accumulate metals (Coughlan et al, 1986), with relatively high concentrations often occurring in the hepatopancreas (Daoji et al, 2004), compared with other metals, lead in the sea is not particularly toxic at concentrations up to 0.8 ppm, lead nitrate even enhances the growth of the diatom *phaeodactylum*.

Fish contain little lead and the content in commercial species in the North sea generally ranges from 0.05-0.5 ppm (wet weight).

1.6. General introduction of Cadmium:

Cadmium is a member of subgroup IIB of the periodic table it is a typical heavy metal, with atomic number 48 and mass number 112.41a.m.u (Weiss et al, 1972, House et al, 2005), Ground State electronic configuration is [Kr]$5s^2 4d^{10}$.

Cadmium is a chemical element with the symbol **Cd** , this metal is chemically similar to the two other stable metals in group IIB, zinc and mercury. Like zinc, it prefers oxidation state +2 in most of its compounds and like mercury it shows a low melting point compared to transition metals. The average concentration of cadmium in the Earth's crust is between 0.1 to 0.5 parts per million (ppm). It was discovered in (Germany in 1817), its name is derived from the Latin word ***Cadmia*** and the Greek word ***Kadmeiathat*** are ancient names for calamine or zinc oxide (S´ergio et al, 2007).

Cadmium is a silvery-white, lustrous, but tarnishable metal; it is soft , ductile and has a relatively high vapour pressure. Cadmium is nearly always divalent; chemically it closely resembles zinc and occurs by isomorphous replacement in almost all zinc ores (Cotton et al, 1972).

1.7. Cadmium in the environment:

Cadmium is a relatively rare element. It is uniformly distributed in the Earth's crust, where it is generally estimated to be present at an average concentration between 0.15 to 0.2 mg/kg (Hiatt et al, 1975, Fleischer et al, 1974).

Cadmium occurs in nature in the form of various inorganic compounds and as complexes with naturally occurring chelating agents; organo-cadmium compounds are extremely unstable and have not been detected in the natural environment (Nordberg, 1974).

Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks, some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing. Although useful applications for cadmium have been recognized only in comparatively recent times, the metals with which it is commonly associated--copper, lead and zinc- have been employed for several thousand years (Friberg, 1974).

The solubility of cadmium in water is influenced to a large degree by the acidity of the medium (Fleischer, 1974). The need to determine cadmium levels in suspended matter and sediments in order to assess the degree of contamination of a water body has been pointed out (Friberg, 1974). Absorbed cadmium accumulates mainly in the renal cortex, liver, the pancreas, thyroid and gall-bladder, testes can also contain relatively high concentrations (World Health Organization, 1974). Several studies suggest that accumulation of cadmium in the human body is a function of age (Schroeder et al, 1961, Piscator et al, 1972).

Cadmium accumulates with age until a maximum level is reached at about age 50; the total body burden of a person of 50 years of age ranges from 5 to 40 mg (Lauwerys, 1978), about half the body burden is found in the kidneys and liver; the cadmium concentration of the cortex of the kidneys ranges from 0.005 to 0.1 mg/g (World Health Organization, 1974), concentrations of cadmium in the renal cortex are normally 5 to 20 times those in the liver (Fleischer, 1974).

Cadmium also consists in the industries as an inevitable by-product of zinc, lead and copper extraction. After being applied it enters the environment mainly through the ground, because it is found in manures and pesticides.

No cadmium ore is mined for the metal, because more than enough is produced as a by-product of the smelting of zinc from its ore sphelerite (ZnS), the main producing country is Canada, with the USA, Australia, Mexico, Japan and Peru also being the major suppliers (Draft, 2008).

1.8. Properties of cadmium:

Cadmium is a lustrous, silver-white, ductile and very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but not in alkalis. It is similar in many respects to zinc but it forms more complex compounds. Cadmium is a soft, malleable, ductile, bluish-white and divalent metal. Unlike other metals, cadmium is resistant to corrosion and as a result it is used as a protective layer when deposited on other metals.

As a bulk metal, cadmium is insoluble in water and is not flammable; however, in its powdered form it may burn and release toxic fumes.

physical properties of cadmium:

Atomic number-48, Atomic mass-112.4 g.mol^{-1}, Electronegativity according to Pauling-1.7, Density-8.7 g.cm^{-3} at 20°C, Melting point-321 °C, Boiling point-767 °C, Vanderwaals radius-0.154 nm, Ionic radius-0.097 nm (+2), Isotopes-15, Electronic shell-[Kr] $4d^{10}$ $5s^{2}$, Energy of first ionization-866 kJ.mol^{-1}, Energy of second ionization-1622 kJ.mol^{-1}, Standard potential-0.402 V and Discovered-Fredrich Stromeyer in 1817 (Holleman et al, 1985, Draft, 2008).

1.9. Industrial and commercial utilization of cadmium:

About three-fourths of cadmium is used in Ni-Cd batteries, most of the remaining one-fourth is used mainly for pigments, coatings, plating and as stabilizers for plastics (Scoullos et al, 2001, Smith et al, 1999).

Cadmium has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against corrosion.

Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission. Cadmium is intentionally added to six major classes of products where it imparts distinct performance advantages and is present as an impurity in five major classes of products where its presence is regarded as an environmental disadvantage but which generally does not affect the performance of the product, cadmium alloys and cadmium electronic compounds such as cadmium telluride (CdTe). The major classes of products where cadmium is present as an impurity are non-ferrous metals (zinc, lead and copper), iron, steel, fossil fuels (coal, oil, gas, peat and wood), cement and phosphate fertilizers (Draft, 2008).

Cadmium emissions in France were reduced by 82% since 1990, explained mainly by improvements in industrial sectors such as iron and steel industry, non-ferrous smelters and removal of pollutants from the flue gases generated by household waste incineration plants (Centre, 2009).

1.10. Toxicity of cadmium:

Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium can greatly increase the cadmium concentration in human bodies. Examples are liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed. Other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air and people that work in the metal refinery industry.

When people breathe in cadmium it can severely damage the lungs, this may even cause death (Draft, 2008). An exposure to significantly higher cadmium levels occurs when people smoke, tobacco smoke transports cadmium into the lungs blood will transport it through the rest of the body where it can increase effects by potentiating cadmium that is already present from cadmium-rich food. The acute oral lethal dose of cadmium for man has not been established; it has been estimated to be several hundred milligrams. Doses as low as 15 to 30 mg (Gleason et al, 1969) from acidic foodstuffs stored in cadmium-lined containers have resulted in acute gastroenteritis (Mckee et al,1963, Fairhall, 1957). Consumption by humans of fluids containing 13 to 15 mg of cadmium per litre has caused vomiting and gastrointestinal cramps (Fulkerson et al,1973).

Acute cadmium poisoning has occurred following exposure to fumes during the melting or pouring of cadmium metal (World Health Organization, 1974), fatalities have resulted from a 5-hour exposure to 8 mg/m^3, although some individuals have recovered after exposure to 11 mg/m^3 for 2 hours (Friberg et al, 1975).

Acute pneumonitis resulted from inhalation of concentrations between 0.5 and 2.5 mg/m^3 for 3 days (Hygienic, 1962), symptoms of acute poisoning include pulmonary oedema, headaches, nausea, vomiting, chills, weakness, and diarrhoea (Spolyar et al, 1944).

The dose of cadmium required to cause symptoms has not been determined. Symptoms of the disease, which occurred most often among elderly women who had many children, are the same as those of osteomalacia (softening of the bone); the syndrome is characterized by lumbar pain, myalgia and spontaneous fractures with skeletal deformation. It is accompanied by the classical renal effects of industrial cadmium poisoning: proteinuria, often glucosuria and aminoaciduria (Friberg et al, 1974). It has been suggested that there is a relationship between chronic ingestion of cadmium and hypertension (Schroeder, 1965); however, data available at the present time are inconclusive (National Institute, 1977), the results of several studies suggest that persons with hypertension have more cadmium and a higher cadmium to zinc ratio in their kidneys than those without hypertension.

In contrast to these findings, no relationship between cardiovascular disease and cadmium levels in the kidney was found in a study of 80 individuals at postmortem (Morgan, 1969).

In addition, no relationship between hypertension and urinary cadmium excretion has been observed (Szadkowski et al, 1969), oral administration of cadmium has produced hypertension in animals. Cadmium is first transported to the liver through the blood, there, it is bond to proteins to form complexes that are transported to the kidneys, cadmium accumulates in kidneys, where it damages filtering mechanisms, this causes the excretion of essential proteins and sugars from the body and further kidney damage, it takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body. Other health effects that can be caused by cadmium are:

- Diarrhoea, stomach pains and severe vomiting.
- Bone fracture.
- Reproductive failure and possibly even infertility.
- Damage to the central nervous system.
- Damage to the immune system.
- Psychological disorders.
- Possibly DNA damage or cancer development.

1.11. Diphenylthiocarbazone:

Diphenylthiocarbazone, H_2D_Z was called (Dithizone) was discovered by Emil fisher, (Fischer, 1878, Fischer, 1882), Dithizone long been used as a reagent for the colorimetric analysis of trace metals (G. Iwantscheff, 1958, E. B. Sandell, 1959).

Twenty-four metal complexes of Dithizone have been prepared, characterized and examined for their photochemical and photochromic under steady illumination with visible light, example of its: $Pd(HD_Z)_2$, $Pt(HD_Z)_2$, $Ag(HD_Z)_2$, $Zn(HD_Z)_2$, $Cd(HD_Z)_2$, $Hg(HD_Z)_2$, $Pb(HD_Z)_2$, $Bi(HD_Z)_2$ and $Bi(HD_Z)_2Cl.2HCl$.

Twenty four metals are capable of reacting with Dithizone to produce colored coordination compounds. Under the proper conditions or upon the removal of all interferences, the reaction can be made selective for a desired substance (Taras et al, 1976).

It is still one of the most important chelating agents used in extraction (Dnnelly et al, 1989). However, it is only recently that evidence has begun to accumulate on the properties and structures of the complexes thus formed (H. Irving et al, 1961, R. F. Bryan et al, 1961). Dithizone is known to an excellent ligand to form complexes even in basic solution (Sang Kim, 2000).

1.11.1. Dithizone properties:

Dithizone is a violet black solid which is insoluble in water below pH 7 (Harris et al, 1999), but is soluble in dilute ammonia solution (Volgel et al, 1975). Dithizone gives green compound when is soluble in non polar organic solvents (Harris et al, 1999), such as chloroform, carbon tetra chloride (Volgel et al, 1975), hexane and benzene (A. Skoog et al, 1976) and it forms red, hydrophobic complexes with most di- and trivalent metal ions (Harris et al, 1999).

Dithizone undergoes oxidation in aqueous solution, whereby concentration of its solution changes. In order to prevent this, hydroxylamine was added and the solutions were kept at less than 10 ˚C (Singh et al, 1989).

Dithizone is widely used for analytical extraction, colorimetric determination of metal ions after analytical extraction and removing traces of metals from aqueous buffer (Harris et al, 1999).

Dithizone in water has the equilibrium:

$$H_2D_Z \xleftrightarrow{H_2O} H^+ + HD_Z^-$$

The neutral molecule H_2D_Z is highly soluble in an organic solvent. The distribution ratio for this molecule between chloroform and water is 2×10^5 (Kenner et al, 1979).

It's known as a reagent for separation of lead and it's photometric determination, but also valuable for Zn, Cd, Hg, Cu and Ag. The great sensitivity of Dithizone reaction arises from high absorptive of Dithizone complexes in the region of 500 to 550 nm (Meriwether et al, 1965).

It must be emphasized that Dithizone is an applicable to quantities of metals in the order. Only the purest Dithizone (e.g. A.R. A analytical Reagent), may be used, since the reagent tends to oxidize to diphenylthiocarbadiazone, $S=C(N=NC_6H_6)_2$.

The latter does not react with metals, and its insoluble in ammonia solution and dissolves in organic solvents to give yellow or brown solution. Reagents for use in Dithizone method of analysis must be highly pure (e.g., S.R. Spectroscopic Reagent) (Vogel et al, 1975).

1.11.2. Structure of Dithizone:

Dithizone contains two active hydrogen atoms, each of which can be replaced by an equivalent of metal, when hydrogen of the Dithizone molecule is replaced, a primary Dithizone is formed: when both are replaced, a secondary Dithizone is formed (Dnnelly et al, 1989).

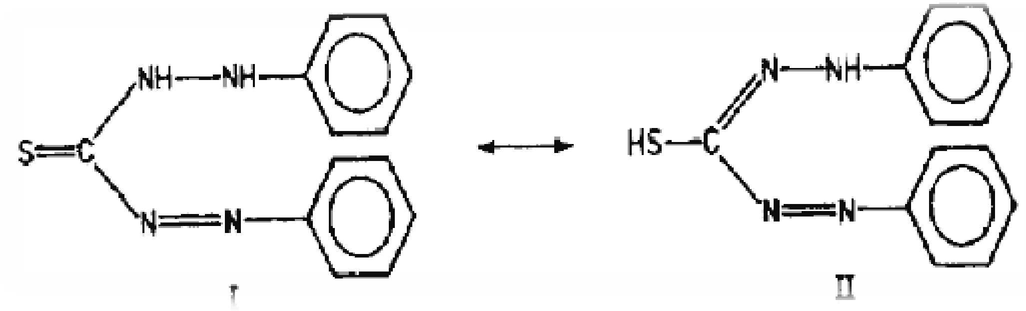

Figure (1.1) Dithizone behaves in solution at autometric mixture of (I) and (II) (Volgel et al, 1975). Function as a monobasic acid (pKa=4.7) up to a pH of about 12: the acid proton is that of the thiol group in (II), Primary metal Dithizonate are formed according to the reaction:

$$M^{n+} + nH_2D_z \leftrightarrow M(HD_z)_n + nH^+$$

Some metals, such as copper, silver, gold, mercury, bismuth and palladium, form a second complex (which we may term ″secondary ″ Dithizonate, which are less stable and less soluble in organic solvent (Volgel et al, 1975).

Dithizone is an excellent reagent for the determination of small (microgram) quantities of many metals and can be made selective for certain metals by resorting to one or more of the following devices:

I- Adjust pH of the solution to be extracted, thus from dilute acid solution (0.1-0.5 N). Silver, mercury, copper, and palladium can be separated from other metals: bismuth can be extracted from a weakly acidic medium; lead and zinc from a neutral or faintly alkaline medium; cadmium form a strongly basic solution containing citrate or tartrate (Volgel et al, 1975).

II- Adding a complex-forming agent or masking agent; the masking agent is reagent that chemically binding an interference and prevents it from causing errors in analysis, e.g. cyanide, thiocyanate, thiosulphate and EDTA (Volgel et al, 1975).

1.12. Separation:

The analyte in most instances is associate with other elements that interfere with its determination (Weiss et al, 1972).

All separation processes have in common the distribution of the components in a mixture between two phases (Skoog et al, 1997), and in the separation of the element in a mixture it is often necessary to;

I- Increase the anaIyte concentration (Mentasti et al, 1989).

II- Eliminate of the matrix interferences during the analysis of the samples.

The most important separation techniques are; extraction, precipitation, ion-exchange, and chromatography (Weiss et al, 1972, Skoog et al, 1997, Mentasti et al, 1989).

1.12.1. Solvent Extraction:

Trace of metals are effectively isolated and concentrated by solvent extraction procedures. The important systems involve are chelation system and ion association system. In chelation system extraction reagent are chosen in order to give colored complexes which can then be used colorimetric determination of the metal ion.

The Dithizone was proved to be the most efficient method for extraction of metals. Other methods which are frequently used are Dithiocarbamate and iodide extraction (Weiss et al, 1972, S´ergio et al, 2007).

The liquid-liquid extraction is a technique in which a solution (usually aqueous) is brought in contact with another solvent (usually organic), essentially immiscible system is product first, in order to transfer one or more solution to the second solvent. The separations are usually simple, clean and rapid. In the chelate extraction system, the metal ion react with a complexing to from a neutral chelate compound.

A chelate compound is a metal-organic compound in which the metal is incorporated into a ring structure with the organic compound. Although a metal-organic chelate can be charged or uncharged, only the uncharged chelate will extract into the organic liquid (Kenner et al, 1979).

Most organic solvents (diethyl ether, ethyl acetate, toluene and methylene chloride) are much less polar than water, polar compounds are more soluble in polar solvents than in non polar solvents. Chloroform is used to extract the colored complex for spectrophotometric measurements (S. Dadfarnia et al, 2002).

Chemical separation techniques have been used both to improve detection limits and to remove interferents (Jiménez et al, 1987). This technique has advantages of relatively easy experimental procedure and good selectivity as well as a disadvantage of low concentration efficiency, thus a preconcentration system has been sometime utilized to enhance the concentration efficiency and to increase the extraction velocity.

Chelating agents used in colorimetry are typically characterized into general groups such as O, O-donating, O, N-donating, N, N-donating and chelating reagent with sulfur functions (K. L. Cheng et al, 1982), they form neutral organic-like complexes that can be extracted into organic solvents (N. Lacy et al, 1999).

After extraction into the organic layer, it is often necessary to return the extracted material to water for the analytical procedure to be used in the determination, this back extraction is known as stripping. For those systems that are pH sensitive, the organic solution is agitated with an aqueous solution that has been adjusted to a pH below the pH range in which the metal is extracted into the organic phase. Sometimes, the organic liquid containing the solute can be agitated with an aqueous solution containing a complexing agent which forms complexes with the metal that are more soluble in water than in the organic liquid used in the extraction (Kenner et al,1979).

1.12.2. pH effect on lead and cadmium extraction:

A large number of interferences may be involved in the extraction of metal chelates from water solution (Kenner et al, 1979), to achieve selective use of masking agent and proper adjustment of pH prior to solvent extraction of the metal complex, many major interferences can be eliminated.

The order of stability of complexes for a limited number of divalent metals has been shown (Christian, 1994).

Pd, Cu, Ni, **Pb**, Co, Zn, **Cd**, Fe, Mn, Mg
←
Increasing of stability

If a solute is an acid or base, its charge changes as the pH is changed. Usually, a neutral species is more soluble in an organic solvent and a charged species is more soluble in aqueous solution (Harris, 1999). Diphenylthiocarbazone, or Dithizone, is a useful reagent separating small quantities of a dozen or more metal ions, its reaction with a divalent cation, such as Pb^{2+}.

The distribution ratio $(C_{Pb})_{org}$ /($C_{Pb})_{aq}$ depends heavily on the concentration of the reactants and also on pH. At low pH values the proportion of metal present as the neutral complex is small and the distribution ratio is correspondingly low. Metal becomes more easily extracted as the pH rises at pH say 3-12 (Sang Kim et al, 2000), appreciable amounts of Dithizone will be present in both phases in the organic phase as neutral H_2Dz and in the aqueous phase primarily as the HDz^- ion (Kenner et al, 1979).

When an uncharged complex forms between a metal ion and an organic chelating reagent, changes in pH can have profound effects on the distribution ratio. For example, Dithizone (H_2Dz) behaves below pH 12 as a monobasic acid with an ionization constant of about 3×10^{-5}.

Both Dithizone H_2D_z and its metal chelates MD_z are essentially insoluble in water but dissolve readily in solvent such as ***chloroform***. Solutions of the reagent are deep green, whereas solutions of the metal chelates are intensely red, violet, orange or yellow depending on the metal chelate and provide a sensitive means for the spectrometric determination of the separated ions.

1.12.3. Mechanism of the formation of Dithizone complex:

In neutral and basic solutions, metal reacts with a solution of Dithizone in presence of chloroform or carbon tetrachloride to form a red colored metal Dithizone. Dithizone chelate are more soluble in chloroform, permitting the extraction of greater amounts of metal (Weiss et al, 1972).

Its well that Dithizone can form stable complexes with many kinds of metal ions (Sang Kim et al, 2000).

The molecular solubility of Dithizone in water is small (pH = 0 to 7) (2×10^{-7}M), but Dithizone dissolves in alkaline aqueous solutions at pH ≥ 12 because of its acidic character (Kolthoff et al, 1969).

Figure (1.2): Reaction of Dithizone with metal ion to from complex (Harris, 1999).

The usual practice is to add the chelate agent to the organic phase. The extraction process can be thought to consist of four equilibrium steps, each with specific equilibrium constant.

First, the complexing (Dithizone) distributes between the aqueous and organic phases:

$$(H_2Dz)_{org} \leftrightarrow (H_2Dz)_{aq} \qquad K_D(H_2Dz) = (H_2Dz)_{org}/(H_2Dz)_{aq}$$

K_D is distribution coefficient of the Dithizone.

Second, the Dithizone in the aqueous phase ionizes:

$$(H_2Dz)_{aq} \leftrightarrow H^+_{aq} + (HDz^-)_{aq} \qquad Ka = [H+]_{aq}[HDz^-]_{aq}/(H_2Dz)$$

Ka is ionization constant of the Dithizone.

Third, the metal ion chelates with the reagent anion to from an uncharged molecule:

$$2HDz^{-} + M^{2+} \leftrightarrow M(HDz^{-})_2 \qquad K_f = [M(HDz)_2]/ [M^{2+}][HDz^{-}]^2$$

K_f is formation constant of the chelate.

Finally, the chelate distributes between the organic and aqueous phase:

$$[M(HDz)_2]_{aq} \leftrightarrow [M(HDz)_2]_{org} \qquad K_D[M(HDz)_2] = [M(HDz)_2]_{aq}/ [M(HDz)_2]_{org}$$

K_D is distribution coefficient of the chelate.

The chelated portion of the metal distributes largely into the organic phase, the metal ion dose not hydrolyzes in the aqueous phase, and the chelate is essentially un dissociated in the non polar organic solvent, the distribution ratio is gives by:

$$D = [MRn]_{org}/ [M^{n+}]_{aq}$$

$$D = M[(HDz)_2]_{org}/ [M^{2+}] = K_{ex}[H_2Dz]^2/ [H_3O^+]^2_{aq}$$

K_{ex} is product of K_D $[H_2Dz]$, K_a, K_f, and K_D $[M(HDz)_2]$.

1.13. Effect of shaking time:

If two phases of extraction system are vigorously agitated, the rate of solvent extraction is usually very high, and in most cases the distribution equilibrium is estimated within 30min, when the extraction is slow, either prolonged two-phases agitation or change in the experimental conditions to achieve the quantitative extraction. Zinc (II), Cobalt (II), Nickel (II), Cadmium (II) and Lead (II) cannot be separated by extraction with dithizone without use of masking agents. However, since the rates of extraction of these metal ions are very different, by shaking the two phases for interval that is necessary to achieve the extraction equilibrium of these metal ions (T. Sekine et al, 1970).

1.14. Preconcentration:

Preconcentration means concentrating a dilute analyte to a level high enough to be analyzed (Harris, 1999). In many cases the available analytical instrumentation does not show enough for the realization of the analysis in these natural samples. As such, a previous step of preconcentration is necessary, for this reason many enrichment procedure have been proposed (Ferreira et al, 1998).

Several analytical techniques. Such as, flame atomic absorption spectrometry (FAAS) (Melo et al, 2000, Anthemidis et al, 2004), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Boevski et al, 2000) and inductively coupled plasma mass spectrometry (ICP-MS) (Álvarez et al, 2001) are available for the determination of trace metals with enough sensitivity for the most applications. Many elements in a seawater even though trace levels are presented at lower level than the detection limits.

Common analytical methods and their determination is spectroscopically and chemically interfered with other major constituents such as NaCl. Much effort has been tried to solve difficulties of such interferences by the development of various techniques (Sturgeon et al, 1980, Boniforti et al, 1984). In order prevent of the interferences, a solvent extraction has been commonly applied for separation of trace elements from the sample matrix (Sang Kim et al, 2000).

Preliminary extraction is still needed for the removal of seawater salts, although direct determination employing matrix modification and Zeeman-effect background correction techniques is now showing promise in some instances (Ediger et al, 1975).

1.15. Sample decomposition methods:

The two types of decomposition method commonly employed for the determination of trace elements in biological and environmental material are:

I- Wet digestion.

II- Dry ashing.

With dry ashing (Muys, 1984, Thornburg, 1982) there is the risk of loss of metal by volatilization of its halides and the temperature has to be kept below 500˚C.

In routine analysis an important consideration is the time taken for the determination and hence a wet digestion procedure was the method of choice (Watson, 1984).

In wet digestion, (Pagenkopf et al,1972, Koirtyohann et al, 1982) concentrated HNO_3 is the most widely used reagent (Bernhard, 1976, May et al,1982).

Although the latter is well accepted, the wet digestion method is more commonly employed with most analytical techniques (Adeloju, 1989).

The preference for this type of decomposition method is based on the reduced danger of losses at the lower operating temperature.

On the other hand, the dry ashing method requires the use of ashing acid and/or careful manipulation of the ashing temperatures to minimize or prevent the loss of analyte (Adeloju et al,1984, Gorsuch, 1970).

The use of relatively larger amounts of reagents in the wet digestion method represents an even greater source for contamination.

The suitability of wet digestion method is frequently investigated for various analytical techniques. Such as, atomic absorption spectrometry, neutron activation analysis fluorimetry and spectrophotometry (Ward et al, 1974).

Several acids and acid mixtures have been used for the digestion of soil samples prior to the analysis of metal, including nitric acid, perchloric acid (1:1)(Agrawal et al, 1980) are claimed to yield high metal recoveries.

Some workers have also used high-pressure digestion in a decomposition vessel or bomb (Halls et al, 1987).

Although many of these procedures are reliable and reproducible, a large proportion of the analysis time is spent at the sample preparation stage (Hsu et al, 1983), Hydrochloric acid (Chow, 1970), perchloric acid (Motto et al, 1970), nitric acid-hydrofluoric acid (1:1) (Ward et al, 1974, Ward et al, 1975) and aqua regia (Berrow et al, 1983), soil usually contains high levels of silicates, in the crystal lattices of which trace amounts of metal salts could be trapped (Connell et al, 1984).

The loss of metal salts due to the evaporation to dryness steps was also studied.

Water, hydrochloric acid, nitric acid, perchloric acid and aqua regia were among the digestion media tested (Connell et al, 1984).

1.16. Marine pollution:

Marine pollution is the introduction by human, directly or indirectly, of marine activities, including fishing; of the quality for the use of seawater, and reduction of amenities (Clark, 2001).

As a cumulative of all kinds of human activity which causes obvious and/or hidden disturbance in the natural structure and functions of water biotic communities, anomalies in their habitats, changes in the hydrology and geomorphology of water bodies, diminishing their fisheries and recreational value, other negative effects of ecological, economic or nature.

High concentration of a toxic compound may kill most or all of the organisms within a particular area where the concentration is sufficiently high (Timbrell, 2002).

The focus is therefore on human, rather than natural inputs to the sea, and on the damaging effects of wastes (Clark, 2001).

These physic-chemical changes affect the degree to which the added substances are available to marine organisms and the effects they have on them (Clark, 2001).

Many substances change their nature when added to seawater; compounds may dissociate or become ionized; metals may change their valence or form complexes with organic molecules; substances may dissolve in seawater, or become adsorbed on to particulate matter and carried to the seabed (Clark, 2001).

Metals have many sources from which they can flow into the seawater body, the most obvious inputs of material to the sea are through pipes discharging directly into it (Clark, 2001), these sources are:

I- Natural sources: metals are found throughout the earth, in rocks, soil and introduce into the water body through natural processes, weathering and erosion.

II- Industrial sources: metals contamination can enter the environment in excess of natural amounts from industrial and mining effluents, from the combustion of fossil fuels (Trefry, 1987).

Metallic compounds which are widely used in other industries as pigments in paint and dye manufacture; in the manufacture of leather, rubber, textiles, paint, paper and chromium factories which are built close to water for shipping.

Inorganic metal arising from a number of industrial and mining sources occurs in water in the +2 oxidation state (Manahan, 2005). New industry, with demands for large volumes of water (for example, for cooling water and waste disposal), have tended to be sited on the coast (Clark, 2001). The concentrations present vary widely according to the geographic location, the type and quantity of industrial influent and the efficiency of removal by treatment plant processes (Yeoman et al, 1989).

Industrial waste comprises a variety of chemicals manufactured and used in industrial processes, and includes pesticides, petroleum product and solvents. Although less than in the past, many such wastes are still discharged into the coastal zone through effluent pipes that disgorge wastes directly into the ocean (Merritts et al, 1998).

III- Domestic wastewater: domestic wastewater contains substantial quantities of metals (Trefry et al,1987). Heavy metals enter wastewater from a variety of domestic and industrial sources (Yeoman et al,1989). Wastewater is a complex mixture of natural inorganic and organic material mixed with man-made substances (Gray, 1999).

Heavy metals released from sewage sludge are distributed throughout the soil system, while remaining in the soil solution as ions and inorganic or organic complexes are mobile for uptake by plants (Nouri et al, 2001). Heavy metals are considered to be one of the main sources of pollution for the environment, since they have an important effect on its ecological quality (Sastre et al, 2002). The human activity increases the contamination levels in the environmental (Di Nezio et al, 2005).

IV- Agricultural sources: residual discharge of agriculture nutrients become polluted also substances on the land. Such as, pesticides and fertilizers applied to crops and washed by rain into rivers and lakes and eventually into the sea (Timbrell, 2002). pathways for metal input to the marine environment include transport via rivers and streams, direct discharge and atmospheric fallout (Trefry et al, 1987).

V- Atmospheric pollution: an important route by which some metals enter the sea is by way of the atmosphere (Clark, 2001). Acid rains containing trace metals input to the water body will cause the pollution of water with metals. In recent years, the amount of air pollution caused by metal has increased considerably due to industrial and car emission (Puchades et al, 1989). Metal is found in the air as find particles that pollute waters and vegetation by settling on them, thus having deleterious effects on humans, most notably children, consuming these items (Boeeckx, 1986, Muys, 1984).

VI- River input: most rivers make a major contribution of metals to the sea, the nature of the input depending on the occurrence of metal and ore-bearing deposits in the catchment area (Clark, 2001). Where a river passes through urban areas, the metal burden is augmented by human wastes and discharges (Clark, 2001). Intense sedimentation in estuaries traps large quantities of metals which become adsorbed on to sediment particles and carried to the bottom (Clark, 2001). An estuary provides a particularly varied chemical environment (Burton et al, 1976, Elderfield, 1978). The annual river water discharge to the ocean system is estimated to be about 3.74×10^{13} m^3 (Baumgartner et al, 1975), which is 2.7×10^{-3} of the total volume of seawater in the world ocean. This river water flow carries approximately 1.5×10^{16} g of particulate matter and 4×10^{15}g dissolved salts per year (Martin et al,1979).

1.17. Physical properties of seawater:

With the advent of portable instruments and test kits capable of providing accurate measurements of seawater quality parameters, the most important advantage of these field techniques is ease of use (Kegley et al,1998).

1.17.1. Dissolved oxygen (DO):

The determination of dissolved oxygen (DO) plays a key role in water pollution control activities and waste treatment process control. In natural and waste waters, DO levels depend on the physical, chemical and biological activities (Pal et al, 1991).

The amount of oxygen dissolved in the water has a profound effect on the plants and animals living in it (Clark, 2001). Plants and animals are all vital to the cleanliness of rivers, all aquatic organisms require oxygen (Gray, 1999).

Organic wastes discharged into water courses and estuaries, the sea are subject to bacterial degradation, which results in the oxidation of organic molecules to stable inorganic compounds. In this process oxygen is consumed and the bacterial population increases (Clark, 2001).

Low levels of dissolved oxygen frequently indicate a high concentration of decaying organic matter in the water. As bacterial digest organic matter, they use up oxygen, leaving little for the other aquatic creatures (Kegley et al, 1998).

There are three factors that affect the inherent solubility of oxygen in water:

I- Temperature as temperature increases, the amount of oxygen (or any gas) dissolved in water decreases (Gray, 1999, Kegley et al, 1998).

II- Partial pressure of oxygen in contact with water the concentration of oxygen in water is directly related to the partial pressure of oxygen in the air that is in contact with the water. The partial pressure of a gas is the fraction of one component (e.g., oxygen) present in a gas mixture (e.g., the atmosphere). Although this is a relatively constant value at sea level, a change to a higher elevation can significantly decrease the amount of available dissolved oxygen (Kegley et al, 1998). An increase in the concentration of dissolved salts lessens the saturation concentration of oxygen which is why seawater has lower saturation levels than freshwater at the same temperature and pressure. A decrease in atmospheric pressure causes a decrease in oxygen (Gray, 1999).

III- Salinity of the water the concentration of salts in water, or salinity, affects how much gas dissolves in water. Typically, the solubility of gases (O_2 and

CO_2) decreases with increasing salinity. This phenomenon plays a major role in regulating how much O_2 and CO_2 are taken up the oceans (Kegley et al, 1998). Salinity is an important measurement in the analysis of certain industrial wastes and seawater (Franson et al, 1981).

1.17.2. Total dissolved solids (TDS):

The total amount of dissolved chemical species is called total dissolved solids, abbreviated TDS, and is a good general measure of the concentration of ionic substances in water (Kegley et al, 1998).

In general, fresh water has less than 1,500 mg/l of TDS, brackish water between 1,500 and 5,000 mg/l TDS, and saline water above 5000 mg/l, seawater has a TDS content of 30,000-40,000 mg/l.

For seawater, where the concentrations of ions are very high, the amount of dissolved solids in solution was expressed as salinity, or milligrams of solids per gram of solution strength (Kegley et al, 1998).

Table (1.1): saturation values of dissolved oxygen as a function of temperature (Kegley et al, 1998).

Temp. (˚C)	DO (mg/l)	Temp. (˚C)	DO (mg/l)	Temp. (˚C)	DO (mg/l)
0	14.62	16	9.87	32	7.31
1	14.22	17	9.67	33	7.18
2	13.83	18	9.47	34	7.07
3	13.46	19	9.28	35	6.95
4	13.11	20	9.09	36	6.84
5	12.77	21	8.92	37	6.73
6	12.45	22	8.74	38	6.62
7	12.14	23	8.58	39	6.52
8	11.84	24	8.42	40	6.41
9	11.56	25	8.26	41	6.31
10	11.29	26	8.11	42	6.21
11	11.03	27	7.97	43	6.12
12	10.78	28	7.83	44	6.02
13	10.54	29	7.69	45	5.93
14	10.31	30	7.56	46	5.84
15	10.08	31	7.43	47	5.74

1.17.3. Conductivity:

The conductance of a solution is (simply the reciprocal of the resistance), is a measure of waters ability to conduct an electric current. This is linked to concentration of mineral salts in solution (Franson et al, 1981).

Conductivity is controlled by the degree to which these salts dissociate into ions. The conductance unit is Siemens S/cm (Gray, 1999, Kegley et al, 1998).

Unpolluted surface water vary in conductivity depending on the underlying geology of the area. The effluent from a wastewater treatment plant may have a high conductivity (300-1000 μS/cm), because of the ionic substances found in treated wastewater Cl^-, Na^+, K^+, PO_4^{-3}, NO_3^- and SO_4^{-2} (Kegley et al, 1998).

1.17.4. Effects of pH:

A decrease in pH much below the neutral value of 7.0 can result in a variety of effects on lakes, rivers, streams and their inhabitants (Kegley et al, 1998).
The solubility of many minerals is increase at lower pH. In areas where there are naturally high concentrations of metal ores, the results is a release of toxic metal ions (e.g., Al^{3+}, Pb^{2+}, etc.) into the environment. Soils are typically composed of aluminosilicates (a variety of compounds containing aluminum, silicon and oxygen).

Which dissolve under acid conditions to release Al^{3+} ions. Aluminum has toxic effects on many plant, animal species and including humans (Kegley et al, 1998).

1- A low pH dissolves the calcium from the shells of crustaceans and mollusks, weakening them and making the animals more susceptible to physical damage as well as to predators and disease (Kegley et al,1998) .
2- Acid disturbs the balance in ion uptake by fish. Fish require a balance of sodium, potassium, calcium and chloride ions in their blood. In acidic water, sodium ions are lost through the gills and cannot be replaced quickly enough to maintain the desired level in the blood. When the balance of ions is disturbed beyond a certain point, the fish dia (Kegley et al, 1998).

1.18. Aim of the study:

I- Estimate levels of Cadmium and Lead along the seawater coast of the city in Benghazi.

II- To compare the results of Lead levels in sea water with the study conducted in 2007.

Experimental:

A step-by-step approach has been taken, through sampling, laboratory cleanliness, per-treatment, extraction, instrumental of measurement, finally, analytical quality control and proper reporting of results.

2.1. Sample collection, preservation and storage:

We collected the samples from different nine positions along extent Benghazi city coast in September-2012. The distance between each point from sampling places about 8 km, each position was taken two water samples and marine soil, show in figure (2.1): Each position was taken five seawater samples and five marine soil samples, then we measured the physical properties of the seawater samples, including (pH, TDS, DO, Salinity and EC), the samples were transported to the laboratory acidification for the seawater samples, then saved in a cold dark place.

Studies have been published on sorption of the sample contents from the container surface (Massee et al, 1981), sample storage (Michnowsky et al, 1982), bottle cleaning methods (Laxen et al, 1981) and filtering the sample, for example, is widely advocated (Batley et al, 1977, Mart, 1979), but this is not the best approach for all studies, as sometimes suspended material should be included in the determination process (Ashton et al, 1987).

In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable analytical results. For certain constituents and physical values, immediate analysis in the field is required in order to obtain dependable results, because the composition of the sample may change before it arrives at the laboratory (Taras et al, 1976).

It is impossible to state unequivocally how much time may be allowed to elapse between collection of a sample and its analysis: this depends upon the character of the sample, the particular analyses to be made, the conditions of storage. Changes caused by the growth of organisms may be greatly retarded by keeping the sample in the dark and at a low temperature until it can be analyzed.

The following maximum limits are suggested as reasonable for samples for physical and chemical analysis:

Unpolluted waters → 72hr
Slightly polluted waters → 48hr
Polluted waters → 12hr

Some determinations are more likely to be affected than others by storage of samples prior to analysis. Certain cations are subject to loss by adsorption on or ion exchange with the walls of glass containers.

Such cations include aluminum, cadmium, chromium, copper, iron, lead, manganese, silver and zinc (Taras et al, 1976), which are best collected in a separate clean bottle and acidified with concentrated hydrochloric or nitric acid to a pH of approximately 3.5 in order to minimize precipitation and adsorption on the walls of the container.

Samples are best analyzed within a few hours of collection, as in this way instability problems are circumvented. If long-term storage is unavoidable then both the method and duration of storage should be evaluated before results on any of these samples are deemed reliable (Massee et al, 1981).

As metals exist in seawater in many more forms other than the simple ionic state, Batley and Gardner's criticisms of the common practice of using samples spiked with solutions of simple metal ions (Batley et al, 1977), would appear to be well justified (US Environmental, 1986). Temperature can change very quickly; pH may change significantly in a matter of minutes; dissolved gases may be lost (oxygen, carbon dioxide, hydrogen sulfide and chlorine) or gained (oxygen and carbon dioxide).

Figure (2.1): Illustration different places of the samples collection on the Benghazi-city.

The different places of the seawater samples collection on the Benghazi-city map, that including the following symbols: P, R, M, G, S, A, N, K and I, see table (2.1). Where:

P: Beside North Benghazi Power Station.

R: Ras-Almaingar Coast.

M: Seaport in front of Higher Court.

G: Giliana Beside Fish Market.

S: Eshbilia (Militarily Resort).

A: In front of Rear Gate of Benghazi University (Alahli Club Beach).

N: Nairoaz Beach.

K: Abou Fakhra Beach.

I: Gamines Beach.

The positions of the marine soil samples in different places on Benghazi city coasts extend give different codes, see table (2.2).

Table (2.1): The positions and codes of the sea water samples in different places for Benghazi city coast:

Position	**Code**
Beside North Benghazi Power Station.	P_1, P_2, P_3, P_4, P_5
Ras-Almaingar Coast.	R_1, R_2, R_3, R_4, R_5
Seaport in front of Higher Court.	M_1, M_2, M_3, M_4, M_5
Giliana Beside Fish Market.	G_1, G_2, G_3, G_4,G_5
Eshbilia (Militarily Resort).	S_1,S_2, S_3, S_4, S_5
In front of Rear Gate of Benghazi University (Alahli Club Beach).	A_1, A_2, A_3, A_4, A_5
Nairoaz Beach.	N_1, N_2, N_3, N_4, N_5
Abou Fakhra Beach.	K_1, K_2, K_3, K_4, K_5
Gamines Beach.	I_1, I_2, I_3, I_4, I_5

Table (2.2): The positions and codes of the marine soil samples for Benghazi city coast:

Position	**Code**
Beside North Benghazi Power Station.	P_1, P_2, P_3, P_4, P_5
Ras-Almaingar Coast.	R_1, R_2, R_3, R_4, R_5
Seaport in front of Higher Court.	M_1, M_2, M_3, M_4, M_5
Giliana Beside Fish Market.	G_1, G_2, G_3, G_4,G_5
Eshbilia (Militarily Resort).	S_1,S_2, S_3, S_4, S_5
In front of Rear Gate of Benghazi University (Alahli Club Beach).	A_1, A_2, A_3, A_4, A_5
Nairoaz Beach.	N_1, N_2, N_3, N_4, N_5
Abou Fakhra Beach.	K_1, K_2, K_3, K_4, K_5
Gamines Beach.	I_1, I_2, I_3, I_4, I_5

2.2. Materials and Reagents:

The following is list of chemicals used throughout this project, the name of the supplier is also given in table (2.3).

Table (2.3): The Chemicals were used in this project:

Chemicals	**Company**
HCl	BDH
Methyl orange indicator	RIEDEL-DE HAËN AG
$NH_2OH.HCl$	BDH
Thymol blue indicator	RIEDEL-DE HAËN AG
KCN	MERCK
Dithizone	RIEDEL-DE HAËN AG
$CHCl_3$	Riedel-deHaën
NH_4OH	PRS
$H_3C_6H_5O_7.H_2O$	RIEDEL-DE HAËN AG
HNO_3	FARMITALIA CARLOERBA
Standard solution of lead	FISONS
Standard solution of cadmium	FISONS
NH_3	RPS
NaOH	MERCK

2.3. Preparation of reagents:

All reagents used in this thesis were analytical-reagent grade, and high-purity deionzed water was used for the preparation of all reagent and metal solutions.

Working solution of lead and cadmium were prepared from standard stock solutions wherever required.

1- Deionzed water: the conductivity was about 0.05µs/cm.
2- Standard lead solution (1000 ppm).
3- Intermediate lead solution: it was prepared by diluting 10.00 ml of the stock solution up to 100 ml using deionzed water (100 ppm).
4- Standard lead solution: it was prepared by diluting 1.00 ml of the intermediate lead solution up to 100 ml using deionzed water (1ppm).
5- Standard cadmium solution (1000 ppm).
6- Intermediate cadmium solution: it was prepared by diluting 10.00 ml of the stock solution up to 100 ml using deionzed water (100 ppm).
7- Standard lead solution: it was prepared by diluting 0.10 ml of the intermediate lead solution up to 100 ml using deionzed water (0.1ppm).
8- Hydroxylamine hydrochloride reagent: it was prepared by dissolving 20.00 g $NH_2OH.HCl$ then diluted up to 100 ml using deionzed water.
9- Thymol blue indicator solution: it was prepared by dissolved 100 mg thymolsulfonephthalein sodium salt then diluted up to 100 ml using deionzed water.
10- Potassium cyanide solution: it was prepared by dissolving 5.00 g KCN then diluted up to 50.00 ml using deionzed water.

CAUTION: Potassium cyanide is extremely poisonous and more than customary precautions should be observed in its handing. Never use mouth pipettes to deliver volumes of cyanide solutions.

11- Dithizone solution: it was prepared by dissolving 0.0050 mg Diphenylthiocarbazone then diluted up to 100 ml using chloroform and the solution should be prepared immediately before use.
12- Ammoniacal cyanide-citrate reagent: it was prepared by dissolving 10.00 g KCN with 500 ml conc. NH_4OH. Then added 10.00 g citric acid $H_3C_6H_6O_7.H_2O$ and diluted up to 1000 ml using deionzed water.
13- Ammonium citric solution: it was prepared by dissolving 22.00 g of citric acid and 4.0 g of hydroxylamine hydrochloride in about 200 ml of deionzed water, and then diluted with ammonium hydroxide in up to 500 ml to bring the pH to 8.5.

2.4. Drying of marine soil samples:

Samples often contain water, either as chemically combined hydrates or as occluded or surface-adsorbed moisture. Most solid materials adsorb atmospheric water on their exposed surface. The amount adsorbed varies with the chemical nature of the solid (Harris et al, 1981), and within wide limits (Fritz et al, 1979).

This water should be removed before the samples are weighed (Harris et al, 1981), and prior to analysis (Harris et al, 1999).

The goal of drying is either to make the sample anhydrous, or to remove adsorbed moisture but retain chemically combined water (Fritz et al, 1979).

Ordinarily, samples are dried in an oven at 105˚C -110˚C or one or two hours (Harris et al, 1999, Harris et al, 1981, Fritz et al, 1979), To constant weight and without sample decomposition (Harris et al, 1981).

2.5. Procedure:

Trace amounts of metals in samples received by the laboratory therefore are not in a form immediately determinable. The purpose of the pre-treatment step is to convert the categories of interest to a measurable form (Ferreira et al, 1998).

2.5.1. Seawater samples treatment:

The method adopted from Berrow and Ure (Bereow et al, 1981) and Paveley and Davies (Paveley et al,1988) for analysis of heavy metal concentrations in soil samples involved aqua regia digestion. Aqua regia (1 part concentrated HNO_3 to 3 part HCl).
(Aksoy et al, 2000).

100 ml of seawater sample was taken, and acidified with excess conc. HNO_3 using methyl orange, and then the volume was reduced to 10.0 ml volume a steam bath 10.0 ml was transferred to a separator funnel, added 10.0 ml ammonium citrate reagent,

2.0 ml hydroxylamine hydrochloride reagent and 5 drops Thymol blue indicator solution.

Conc. NH_4OH Was added to make it alkaline. 4.0 ml KCN solution was carefully added and the pH adjusted to 8-9 with 1% HNO_3.

Then shaken vigorously for 30 min. with 5.0 ml portions Dithizone solution until the color in the last portion remains unchanged.

While in case of FAAS, the $CHCl_3$ extract was transferred into another separator funnel, and 10 ml 1% HNO_3 was added. The mixture was shaking for 30 min. and allowed to the layers for separate, and then lead content in the aqueous phase was measured using FAAS.

2.5.2. Digestion of marine soil samples:

10 g of sample was placed into 250 ml beaker, then 2.5 ml of (36%) conc. hydrochloric acid was added and the mixture was evaporated to dryness by heating on a hot-plate. This procedure was repeated with two additions of 2.5 ml conc. HCl, cooling the beaker for about 2min. between each addition. Then added 2.5 ml conc. Nitric acid (65%) and heated on a hot plate at approximately 290˚C until nitrogen oxide fumes are just given off cool the beaker again for about 2 min. after evaporated to dryness.

After cooling, the residue was heated to 40-50˚C with 75.0 ml of 1M HCl and the mixture was filtered through (Whatman 52) filter paper into 100 ml volumetric flask. The filter paper was rinsed with a small volume of 1M HCl and the volume was made up to 100 ml by adding redistilled water into the flask. 10.0 ml from this solution was transferred to a separator funnel, added 10.0 ml ammonium citrate reagent, 2.0 ml hydroxylamine hydrochloride reagent, and 5 drops Thymol blue indicator solution.

Conc. NH_4OH Was added to make it alkaline. 4.0 ml KCN solution was carefully added and the pH adjusted to 8-9 with 1% HNO_3.

Then shaken vigorously for 30 min. with 5.0 ml portions Dithizone solution until the color in the last portion remains unchanged.

While in case of FAAS, the $CHCl_3$ extract was transferred into another separator funnel, and 10 ml 1% HNO_3 was added. The mixture was shaking for 30 min. and allowed to the layers for separate, and then metals content in the aqueous phase was measured using FAAS.

2.6. Instruments:

Lead and cadmium concentrations were determined by flame atomic absorption spectrometer model nov AA300. All absorbance measurements were made, Pb at 283.3 nm wavelength using a lead hollow cathode lamp with 3.0 mA current, but Cd at 228.8 nm wavelength using a cadmium hollow cathode lamp with 4.0 mA current.

Digital pH meter (JENWAY mode 3150) was used to measure the pH of the solutions. Dissolved oxygen meter (CORNING).

Conductivity meter and Total Dissolved Solids meter (CORNING).

(I) (II) (II)

Figure (2.2): (I) Photograph of the pH meter and (II) Conductivity meter.

2.6.1. Single beam atomic absorption spectrometer:

Atomic spectroscopy is used for the qualitative and quantitative determination of perhaps 70 elements. Sensitivities of atomic methods lie typically in the parts-per-million (Skoog et al,1997) to parts-per-billion range (Harris et al,1999, Skoog et al,1997). Atomic absorption spectrophotometer (AAS) is an extremely versatile analytical tool. The technique of AAS is used to determine the concentration of trace quantities of metals in a sample (Kegley et al, 1998), as free cations or as cations that are closely associated with specific anions (Kegley et al, 1998). Flame atomic absorption spectrometry (FAAS) is a mature analytical method, which is present in almost any analytical laboratory as a working horse for elemental determinations of elemental metals (Nabil et al, 2012). Since its development in the late 1950 s. Atomic absorption spectroscopy has been one of the fastest growing analytical tools (Weiss et al,1972). Speed, convenience, unusually high selectivity (Harris et al,1999, Skoog et al,1997) and moderate instrument costs (Skoog et al,1997). Spectroscopic determinations of atomic species can only be performed on a gaseous medium of the elements (Skoog et al,1997). Samples are vaporized at 2000-6000 K and atomic concentrations are determined by measuring absorption or emission at characteristic wavelengths (Harris et al,1999). Lead has been determined by atomic absorption in many different materials. Three absorption lines can be used, the most sensitive being at 217.0 nm. The monochromator does not extend to the end of the UV range; the 283.3 nm line should be used, which is somewhat less sensitive, for higher concentrations of lead, and cadmium at 228.8 nm (Weiss et al,1972). Most atomic absorption measurements are made with instruments equipped with an ultraviolet/visible grating monochromator (Skoog et al,1997).

Figure (2.3): Photograph of the nov AA 300 atomic absorption spectrometers assembled in the laboratory of chemistry department.

The flame is located between a radiation source of optimum wavelength and a detector in a manner analogous to a spectrophotometric cell.

The sample solution is first drawn into the burner-nebulizer by a stream of air or other oxidant such as nitrous oxide, and then mixed with fuel. Most of the sample solution passes into the nebulizer chamber as relatively large droplets that settle and then pass down the drain tube (Kenner et al, 1979).

The remaining solution is carried by the air-fuel mixture as a mist to the burner head, where the solvent evaporates and the solute is dissociated into atoms by the heat of the flame.

The number of atoms reaching this point in the operation constitutes only a small fraction of the total. For high sensitivity, as many as possible of these atoms present in the flame should absorb radiation from the source (Kenner et al, 1979).

The ideal source for this purpose should be of high intensity at the wavelength needed for the element being determined, and of low intensity at all other wavelength. The nearest approach to this ideal is a lamp whose cathode contains the element being determined.

On being heated, atoms of this element emit energy at the wavelength most likely to be absorbed by that same element in the flame (Kenner et al, 1979).

2.6.1.1. Hollow cathode lamp:

The most common and useful radiation source for atomic absorption measurements is the hollow cathode lamp (HCL) (Skoog et al,1997).

Monochromator cannot isolate lines narrower than 10^{-3} to 10^{-2} nm. To product narrow lines of the correct frequency, we use a hollow-cathode lamp containing a vapor of the same element as that being analyzed (Harris et al, 1999). A hollow-cathode lamp, such as that shown in figure (2.5), is filled with Ne or Ar at a pressure of ~ 130-700 Pa (1-5 torr) (Harris et al, 1999). Ionization of the inert gas occur when a potential on the order of 300V is applied across the electrodes, which generates a current of about 5 to 15 mA as ions and electrons migrate to the electrodes (Skoog et al, 1998).

When a high voltage is applied between the anode and cathode, when the filler gas is ionized and positive ions are accelerated toward the cathode. They strike the cathode with enough to "sputter" metal atoms from the cathode into the gas phase.

The free atoms are excited by collisions with high-energy electrons and then emit photons to return to the ground state. This atomic radiation has the same frequency as that absorbed by analyte atoms in the flame or furnace (Harris et al, 1999).

Hollow-cathode lamps for about 40 elements are available for commercial sources. Some are with a cathode containing more than one element; such lamps provide spectral lines for the determination of several species.

The development of the hollow-cathode lamp is widely regarded as the single most important event in the evolution of atomic absorption spectroscopy (Skoog et al,1997).

Figure (2.4): Photograph of Hollow Cathode lamp of lead metal.

Figure (2.5): Photograph of Hollow Cathode lamp of cadmium metal.

2.6.1.2. Background correction:

Unlike ordinary spectrophotometers, those used in atomic spectroscopy must incorporate background correction to distinguish analyte signal from absorption, emission (Harris et al, 1999). For atomic absorption, beam chopping or electrical modulation of the hollow-cathode lamp (pulsing it on and off) are used to distinguish the signal of the flame from the desired atomic line at the same wavelength. For deuterium lamp alternation with that from the hollow-cathode. The monochromator bandwidth is so wide that a negligible fraction of D_2 radiation is absorbed by the analyte atomic absorption line. Light from the hollow-cathode lamp is absorbed by analyte, absorbed and scattered by background. Light from the D_2 lamp is absorbed and scattered only by background.

The difference between absorbance measured with the hollow-cathode and absorbance measured with the D_2 lamp is the absorbance due to analyte.

2.6.1.3. Interferences:

Interferences is any effect that change the signal while analyte concentration remains unchanged. In atomic spectroscopy, interference is widespread. It may be corrected by counteracting the source of interference or by preparing standard that exhibit the same interference (Harris et al, 1999).

I- Spectral interferences:

Refers to the overlap of analyte signal with signals due to other elements or molecules in the sample or with signals due to the flame or furnace (Harris et al, 1999). Interference due to overlapping lines is rare because the emission lines of hollow-cathode sources are so very narrow.

Such interference can occur if the separation between two lines is on the order of 0.01 nm (Skoog et al, 1997). Interference from the flame can be subtracted by using D_2 background correction.

The best means of dealing with overlap between lines of different elements in the sample is to choose another wavelength for analysis (Harris et al, 1999).

Elements that form very stable diatomic oxides are incompletely atomized at the temperature of the flame or furnace.

The spectrum of a molecule is much broader and more complex than that of an atom, because vibrational and rotational transitions are combined with electronic transitions (Harris et al, 1999).

II- Chemical interferences:

Chemical interferences in AAS are caused by reactions between the analyte and the interferents that decrease the analyte concentration in the flame (Skoog et al, 1997).

Which caused by any component of the sample that decrease the extent of atomization of analyte (Harris et al, 1999). For example $SO4^{2-}$ and $PO4^{3-}$ prevent the atomization of Ca^{2+}, perhaps by forming nonvolatile salts. Releasing agents are chemicals that can be added to a sample to decrease chemical interference. EDTA and 8-hydroxyquinoline protect Ca^{2+} from the interfering effects of $SO4^{2-}$ and $PO4^{3-}$.

La^{3+} can also be used as a releasing agent, apparently because is preferentially reacts with $PO4^{3-}$ and frees the Ca^{2+}. A fuel-rich flame is recommended to reduce certain oxidized analyte species that would otherwise prevent atomization. Higher flame temperatures eliminate many kinds of chemical interference (Harris et al, 1999).

III- Ionization interferences:

The ionization of atoms and molecules which is usually inconsequential in combustion mixtures that involve air as the oxidant (Skoog et al, 1997). Can be a problem in the analysis of alkali metals at relatively low flame temperature and in the analyses of other elements at higher temperature (Harris et al, 1999).

Because the alkali metals have the lowest ionization potentials, they are most extensively ionized in a flame.

So ionization of the analyte ions leads to low results (Skoog et al, 1997). At 2450K and a pressure of 0.1Pa, sodium is 5% ionized. With its lower ionization potential, potassium is 33% ionized under the same conditions.

Because ionized atoms have energy levels different from those of neutral atoms, the desired signal is desreased (Harris et al, 1999). The errors caused by analyte ionization can frequently by eliminated by addition of an ionization suppressor, which provides a relatively high concentration of electrons to the flame: suppression of analyte ionization results. Potassium salts are frequently used as ionization suppressors because of the low ionization energy of the element (Skoog et al, 1997).

IV- Physical interferences:

Most parameters that affect the rate of sample uptake in the burner and the atomization efficiency can be considered physical interferences.

This includes such things as variations in the gas flow rates, variation in sample viscosity due to temperature, solvent variation, high solids content and changes in the flame temperature (Christian et al, 1994).

2.7. The calibration curve for lead using FAAS:

Standard solutions of concentration 0.00, 1.00, 2.00, 3.00, 4.00, 5.00 ppm, were prepared from the 100 ppm stock solution and diluted with deionzed water in 100 ml volumetric flask.

Table (2.4): Calibration curve of standard lead solutions (0.00, 1.00, 2.00, 3.00, 4.00, and 5.00 mg/l) at 25˚C (n=4) using flame atomic absorption spectroscopy.

Concentration (mg/l)	Absorption	±SEM
0.00	0.00005	0.000077
1.00	0.01273	0.000087
2.00	0.02476	0.000252
3.00	0.03717	0.000135
4.00	0.04888	0.000068
5.00	0.06014	0.000420

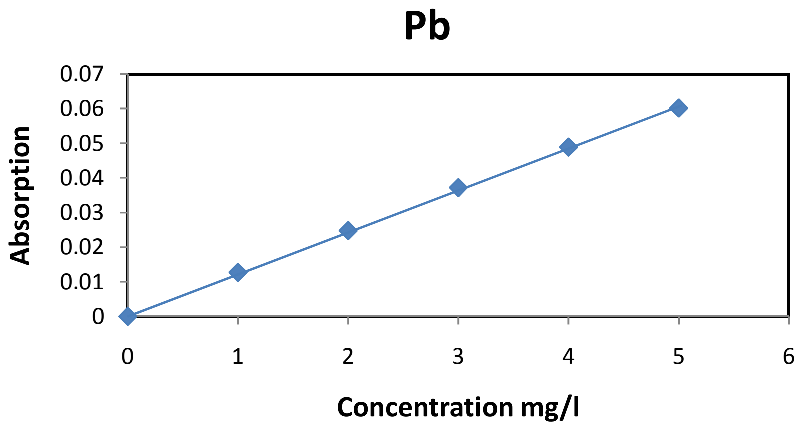

Figure (2.6): The Calibration Curve for Lead using FAAS.

Table (2.5): Calibration Function of lead.

Slope	0.01205 A.L/mg	**R^2-adjusted**	0.999319504
Detection limit	0.04227 mg/l	--	--

A typical Beer´s law plots, calibration curve, are shown in figure (2.6). Even when there is full confidence that Beer´s law can be applied, there are of course, random errors in absorbance measurement could be considered. Random instrumental errors arise primarily from electronic and hence, vary somewhat with instrument design (Kegley et al, 1998).

Table (2.6): Data of adjust spectrometer of Lead:

Wavelength line	283.3 nm	**Slit width**	1.2 nm
Lamp current	3.0 mA	**Peak smoothing**	20/25
Integr. time	3.0 sec.	**Analytical mode**	Single beam

Table (2.7): Data of adjust the flame of Lead:

Flame	C_2H_2/air	**Burner type**	50 mm
burner	9mm	**Nebulizer rate**	5.0 ml/min

2.8. The calibration curve for Cadmium using FAAS:

Table (2.8): Calibration curve of standard Cadmium solutions (0.00, 0.100, 0.200, 0.300, 0.400, and 0.500 mg/l) at 25˚C (n=4) using flame atomic absorption spectroscopy:

Concentration (mg/l)	Absorption	±SEM
0.000	0.000460	0.000066
0.100	0.01695	0.000165
0.200	0.03291	0.000359
0.300	0.04824	0.000237
0.400	0.06309	0.000164
0.500	0.07810	0.000764

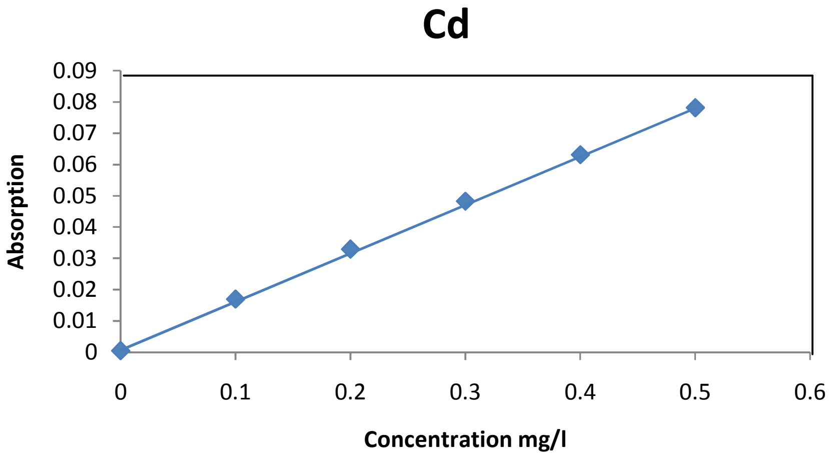

Figure (2.7): The calibration curve for Cadmium using FAAS.

Table (2.9): Calibration Function of Cadmium:

Slope	0.16576 A.L/mg	**R^2-adjusted**	0.999944493
Detection limit	0.00114	--	--

Table (2.10): Data of adjust spectrometer of Cadmium:

Wavelength line	228.8 nm	**Slit width**	0.5 nm
Lamp current	4.0 mA	**Peak smoothing**	20/25
Integr. time	3.0 sec.	**Analytical mode**	Single beam

Table (2.11): Data of adjust the flame of Cadmium:

Flame	C_2H_2/air	**Burner type**	50 mm
burner	9mm	**Nebulizer rate**	5.0 ml/min

Results and discussion:

The parameters that influence the efficient extraction of small quantities of lead and cadmium metals in seawater and marine soil samples were discussed in this chapter which included (pH, shaking time, stability and preconcentration). The results obtained were presented in a tables and figures.

3.1. Physical properties of seawater samples:

All living organisms require a wide variety of inorganic compounds for growth, repair, maintenance and reproduction. Water is one of most important, as well as one of the most abundant, of these compounds, it is particularly vital to microorganisms.

It is possible to obtain a field measurement of the total concentration of just the ionic components in solution by taking advantage of the fact that ions are charged species.

A solution containing charged species will act as a conductor and permit the flow of electricity through the solution. The amount of current that flows is proportional to the concentration and types of dissolved ions in solution.

Conductivity is the quantity that is usually recorded as a measure of total dissolved solids. The total amount of dissolved chemical species in water is called total dissolved solids, abbreviated TDS, is a good general measure of the concentration of ionic substances in water.

In general, seawater has a TDS content of 30-40 g/l. Where, from the results obtained found that ranging between (25.1-29.8 mg/l) in different of places of Benghazi-city coast.

The oxygen is only slightly soluble in water. When an aquatic solution is saturated with air at 1 atmosphere and 25˚C, the amount of oxygen present in the solution is only 8.32 mg/l. The amount of dissolved oxygen in a body of water must be above a certain level to sustain life, with most fish requiring at least 5-6 mg/l of DO for survival (Kegley et al, 1998). The utilization of organic matter in water by microorganisms requires oxygen for the biochemical metabolic processes that occur and when the concentration of organic matter is high, the dissolved oxygen in the water is used up by rapidly growing microorganisms, leaving little oxygen for use by the fish and other aquatic organisms such as the zooplankton. So the algae die and the bacteria that degrade the algae use up all available oxygen. There are also processes that can increase the level of DO above the saturation concentration for a particular temperature. The most important of these is photosynthesis by algae.

During periods of rapid algae growth, oxygen is produced so quickly that it cannot be dissipated fast enough to maintain saturation levels of oxygen in the water.

The result is a body of water that is supersaturated with oxygen, that is, the concentration of dissolved oxygen is above the equilibrium value. Water in which an algal bloom is in full swing will often appear to "fizz" as dissolved oxygen escapes from the water on a sunny day.

Plant and animals are all vital to the cleanliness of rivers, and all aquatic organisms require oxygen. The solubility of oxygen depends on three factors, the pressure, temperature and the concentration of dissolved minerals in the water.

Table (3.1): Physical properties of Benghazi city coast seawater samples beside North Benghazi Power Station.

code	**EC mS/cm**	**TDS g/l**	**DO mg/l**	**pH**	**T ˚C**	**Salinity**
P_1	52.5	26.5	8.08	7.69	25.6	35.2
P_2	52.6	26.5	8.08	7.70	25.6	35.3
P_3	52.7	26.6	8.07	7.69	25.6	35.3
P_4	52.8	26.6	8.07	7.60	25.5	35.3
P_5	52.8	26.7	8.07	7.70	25.7	35.3
Mean	52.7	26.6	8.07	7.86	25.6	35.3

Table (3.2): Physical properties of the seawater samples Ras-Almaingar coast.

code	**EC mS/cm**	**TDS g/l**	**DO mg/l**	**pH**	**T ˚C**	**Salinity**
R_1	50.0	25.1	8.12	7.24	26.8	33.0
R_2	49.7	25.4	8.11	7.23	26.7	33.9
R_3	50.1	25.5	8.11	7.24	26.8	34.0
R_4	50.2	25.6	8.10	7.23	26.7	34.1
R_5	50.6	25.7	8.10	7.26	26.8	34.1
Mean	50.12	25.5	8.11	7.24	26.8	33.8

Table (3.3): Physical properties of the seawater samples near seaport front of Higher Court.

code	**EC mS/cm**	**TDS g/l**	**DO mg/l**	**pH**	**T °C**	**Salinity**
M_1	56.7	28.4	8.11	7.71	27.4	37.9
M_2	56.1	28.1	8.11	7.72	27.5	37.4
M_3	56.2	28.1	8.12	7.73	27.5	37.4
M_4	56.3	28.1	8.11	7.75	27.3	37.4
M_5	56.3	28.1	8.10	7.75	27.4	37.4
Mean	56.3	28.2	8.11	7.73	27.4	37.5

Table (3.4): Physical properties of the seawater samples for Giliana coast.

code	**EC mS/cm**	**TDS g/l**	**DO mg/l**	**pH**	**T °C**	**Salinity**
G_1	58.6	29.4	8.12	7.52	28.1	39.2
G_2	57.3	28.7	8.12	7.64	27.7	38.3
G_3	57.2	28.6	8.12	7.66	27.6	38.2
G_4	56.9	28.6	8.12	7.68	27.6	38.0
G_5	57.1	28.6	8.12	7.68	27.5	38.0
Mean	57.4	28.8	8.12	7.64	27.7	38.3

Table (3.5): Physical properties of the seawater samples for Eshbilia coast (Militarily resort).

code	EC mS/cm	TDS g/l	DO mg/l	pH	T ˚C	Salinity
S_1	56.7	28.5	8.11	7.69	28.8	38.1
S_2	55.6	27.9	8.11	7.73	28.8	37.2
S_3	45.9	27.5	8.11	7.61	29.0	36.5
S_4	55.3	27.8	8.10	7.70	29.1	37.0
S_5	55.4	27.8	8.12	7.70	28.6	37.0
Mean	53.8	27.9	8.11	7.69	28.9	37.2

Table (3.6): Physical properties of the Alahli Club beach seawater samples (In front of Real Gate of Benghazi University).

Code	EC mS/cm	TDS mg/l	DO mg/l	pH	T ˚C	Salinity
A_1	60.2	29.8	8.12	7.59	28.3	39.6
A_2	58.8	29.2	8.11	7.59	28.0	38.8
A_3	58.0	29.1	8.12	7.58	27.3	38.7
A_4	57.7	28.9	8.12	7.62	27.3	38.6
A_5	58.2	29.0	8.12	7.62	27.5	38.6
Mean	58.58	29.2	8.12	7.60	27.68	38.86

The results of salinity of the Alahli Club are highest, and lead concentrations in this area are highest. So, the relationship between salinity and cation concentrations it is directly proportional, also the EC and TDS, but at Ras-Almaingar coast the salinity, EC and TDS are lowest, as well lead concentration is smallest.

Table (3.7): Physical properties of the Nairoaz beach seawater samples.

Code	**EC mS/cm**	**TDS mg/l**	**DO mg/l**	**pH**	**T ˚C**	**Salinity**
N_1	57.1	28.8	8.12	7.78	29.8	38.1
N_2	56.9	28.6	8.12	7.78	29.5	38.1
N_3	57.1	28.6	8.13	7.82	29.4	38.1
N_4	57.1	28.7	8.12	7.85	29.4	38.1
N_5	57.0	28.5	8.12	7.81	29.3	38.0
Mean	57.0	28.6	8.12	7.81	29.5	38.1

Table (3.8): Physical properties of the seawater samples Abou Fakhra coast.

code	**EC mS/cm**	**TDS mg/l**	**DO mg/l**	**pH**	**T ˚C**	**Salinity**
K_1	60.2	29.8	8.12	7.58	28.7	39.6
K_2	58.4	29.2	8.12	7.57	28.3	38.8
K_3	58.0	29.1	8.14	7.57	28.0	38.7
K_4	57.9	29.0	8.13	7.57	28.0	38.5
K_5	58.3	29.0	8.12	7.59	27.8	38.6
Mean	58.6	29.2	8.13	7.58	28.2	38.8

The organic wastes discharged into water courses and estuaries, and the sea are subject to bacterial degradation. In this process oxygen is consumed and the bacterial population increases (Clark, 2001).

The determination of dissolved oxygen (DO) plays role in seawater pollution control activities and waste treatment process control (pal et al, 1991). All results of DO are almost equal and at normal range, due to all sewage discharge pipes blocked along the coast of the city of Benghazi.

Table (3.9): Physical properties of the Geminis coast seawater samples.

code	EC mS/cm	TDS mg/l	DO mg/l	pH	T ˚C	Salinity
I_1	57.7	29.3	8.12	7.19	29.5	38.9
I_2	58.2	29.3	8.12	7.45	28.5	38.9
I_3	58.6	29.3	8.12	7.46	28.3	38.9
I_4	58.5	29.3	8.12	7.47	28.3	38.4
I_5	58.7	29.3	8.12	7.48	28.5	38.5
Mean	58.3	29.3	8.12	7.41	28.6	38.7

Where, from the results obtained found that ranging DO was between (8.07-8.14mg/l) in different of places of Benghazi-city coast see above tables. The majority of water is slightly basic due to the presence of carbonate and bicarbonate.

A departure from the norm for given water could be caused by the entry of strongly acidic or basic industrial wastes (Gray, 1999). An organism must maintain a constant balance of acids and bases to remain healthy. Biochemical reactions in living systems are extremely sensitive to even small changes in the acidity or alkalinity of the environments in which they occur. In fact, H^+ and OH^- are involved in almost all biochemical processes, the functions of a cell are modified greatly by any deviation from its narrow band of normal H^+ and OH^- concentrations. For this reason, the acids and bases that are continually formed in an organism must be kept in balance (Tortora et al, 2002).

As a living organism takes up nutrients, carries out chemical reactions and excretes wastes, its balance of acids and bases tends to change, and the pH fluctuates.
pH in our environments water and soil can be altered by waste products from organisms, pollutant from industry or fertilizers used in agricultural field or gardens.

When bacteria are grown in a laboratory medium, they excrete waste products such as acids that can alter the pH of the medium. If this effect were to continue, the medium would become acidic enough to inhibit bacterial enzymes and cause the death of the bacteria.

To prevent this problem, pH buffers are added to the culture medium (Tortora et al, 2002). Most organisms grow best in environments with a pH value between 6.5 and 8.5. Among microbes and fungi are best able to tolerate acidic conditions (Tortora et al, 2002).

The pH of natural waters has major consequences for the organisms that live there. Acidification is a particular problem, because more human inputs into neutral systems are acidic than basic.

A decrease in pH much below the neutral value of 7.0 can result in a variety of effects on lakes, rivers, streams and their inhabitants (Kegley et al, 1998).
Where, from the results obtained found that ranging pH was (7.19-7.86) in different of places of Benghazi-city coast see above tables. Seawater is water from a sea or ocean.

On average, seawater in the world's oceans has a salinity of about 3.5% (35 g/L, or 599 mM). From the results obtained it's found salinity was (33.0-39.6) in different, Benghazi-city coast and that's mean it's in range see above tables.

3.2. Effect of pH for Metals-Dithizone complex:

The formation of metal-Dithizone complex was influenced by solution pH for Pb and Cd (II) ions. Increase of pH effect on the allow the reaction of Dithizone with other metallic cation, the pH effect on the extraction of metals was studied.

The pH controlled with certain limits to obtain optimum, reproducible color formation. The results demonstrated that the completeness extraction of metal-Dithizone complex lies between pH 3-12 and maximum absorbance was at pH 7-9 (Sang Kim et al, 2000), see figure (3.2), and this agree with our pH choose for metal-Dithizone complex and it clears from the figure (3.1), the maximum absorption was at pH 7-9 and that’s why we choose this region.

Table (3.10): The relation between the pH and the mean absorbance standard solution of lead and Cadmium 1ppm, (n=4) at 25˚C, using FAAS.

pH	Lead Absorption	Cadmium Absorption
3	0.181	0.220
4	0.181	0.270
5	0.315	0.341
6	0.320	0.345
7	0.341	0.405
8	0.330	0.375
9	0.325	0.330
10	0.310	0.322
11	0.315	0.311
12	0.210	0.300

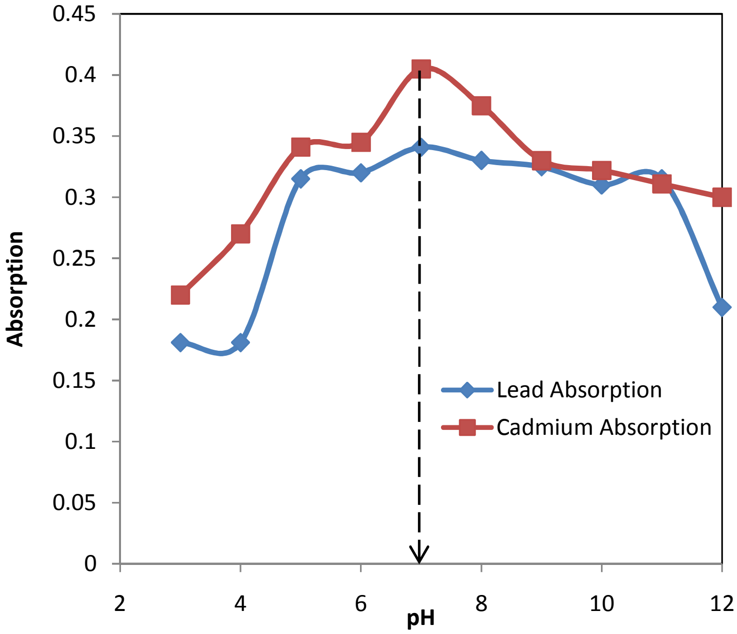

Figure (3.1): Effects of pH for the extraction of Cd and Pb using FAAS

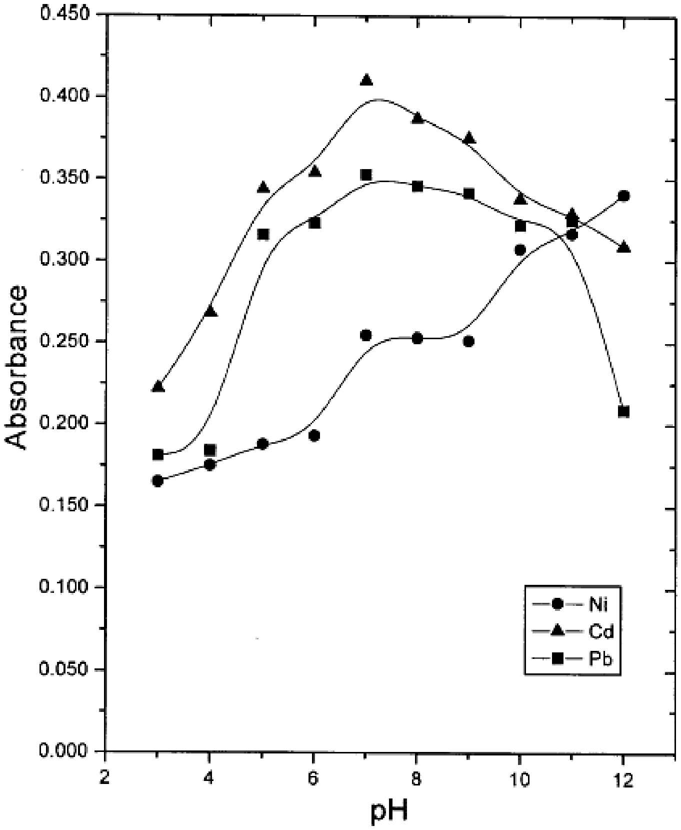

Figure (3.2): Effects of pH for the extraction of Cd and Pb using AAS (Sang Kim et al, 2000):

3.3. Effect of shaking time and stability:

The solution was shaken by a mechanical shaker (Stuart Scientific, UK) for the formation of complexes to be extracted effectively. The absorbances were measured in the back-extracted solution by changing shaking time from 10 min to 120 min. The constant extractions could be obtained by shaking the solution more than 30 min. (Sang Kim et al, 2000).

3.4. Determination of metals (Cd and Pb) in seawater and marine soil samples:

3.4.1. Determination of Lead:

Results of the analysis for seawater and marine soil samples taken from different places were shown in the following tables:

Table (3.11): Concentration of Lead in seawater samples from Benghazi City Coast beside North Benghazi Power Station (P), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
P_1	0.000371	51.72	0.05346
P_2	0.000853	88.71	0.05128
P_3	0.000593	68.80	0.04927
P_4	0.000737	79.83	0.05717
P_5	0.000630	72.26	0.05175

Table (3.12): Concentration of Lead in marine soil samples from Benghazi City Coast beside North Benghazi Power Station (P), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
P'_1	0.005001	387.9	0.08934
P'_2	0.005181	390.7	0.08922
P'_3	0.005226	394.4	0.08231
P'_4	0.005267	397.8	0.08911
P'_5	0.004917	368.8	0.08822

Table (3.11) showed the values of lead concentration in seawater samples were lower than marine soil samples in table (3.12); this is due to the accumulation of lead metal in soil.

Table (3.13): Concentration of lead in seawater samples from Ras-Almaingar Coast (R), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
R_1	0.003072	52.27	0.09330
R_2	0.003112	53.30	0.09334
R_3	0.003923	58.81	0.09232
R_4	0.003341	55.67	0.09541
R_5	0.004011	61.21	0.09321

Table (3.14): Concentration of lead in marine soil samples from Ras-Almaingar Coast (R), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
R'_1	0.004230	311.8	0.09109
R'_2	0.004016	294.0	0.09112
R'_3	0.003710	268.6	0.09132
R'_4	0.004405	326.2	0.09321
R'_5	0.004010	300.1	0.09123

Table (3.13) showed the values of lead concentration in seawater samples were lower than marine soil samples in table (3.14); this is due to the high density of lead metal.

Table (3.15): Concentration of lead in seawater samples from near Seaport in front of Higher Court (M), (n=4), using FAAS.

Symbol	Flame Atomic Absorption Spectroscopy		
	Absorption	**Conc. (µg/l)**	**±SEM**
M_1	0.001508	139.0	0.05251
M_2	0.001762	158.6	0.04997
M_3	0.001513	139.4	0.05221
M_4	0.001505	138.8	0.05091
M_5	0.001574	144.0	0.04980

Table (3.16): Concentration of lead in marine soil samples from near Seaport in front of Higher Court (M), (n=4), using FAAS.

Symbol	Flame Atomic Absorption Spectroscopy		
	Absorption	**Conc. (mg/kg)**	**±SEM**
M'_1	0.005684	432.4	0.08829
M'_2	0.005581	423.8	0.08822
M'_3	0.006128	469.2	0.08234
M'_4	0.005780	440.3	0.08431
M'_5	0.005789	441.4	0.08424

Table (3.15) showed the values of lead concentration in seawater samples were lower than marine soil samples in table (3.16); this is due to the accumulation of lead metal in soil.

Table (3.17): Concentration of lead in seawater samples from Giliana Coast (G), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
G_1	0.000787	83.66	0.05237
G_2	0.001020	101.5	0.05111
G_3	0.001032	102.5	0.04998
G_4	0.000816	85.91	0.05050
G_5	0.000887	93.39	0.05116

Table (3.18): Concentration of lead in marine soil samples from Giliana Coast (G), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
G'_1	0.003546	255.0	0.09262
G'_2	0.003386	241.6	0.09321
G'_3	0.003410	243.7	0.09433
G'_4	0.003531	253.3	0.09561
G'_5	0.003526	253.1	0.09342

Table (3.19): Concentration of lead in seawater samples from Eshbilia (Soldiery Resort) coast (S), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
S_1	0.000932	94.83	0.05339
S_2	0.000766	82.07	0.05451
S_3	0.000755	81.24	0.05134
S_4	0.000987	99.02	0.05460
S_5	0.000818	89.29	0.05128

Table (3.20): Concentration of lead in marine soil samples from Eshbilia (Soldiery Resort) coast (S), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
S'_1	0.004160	306.0	0.09097
S'_2	0.003924	286.4	0.09189
S'_3	0.004201	309.3	0.09321
S'_4	0.004349	321.7	0.09432
S'_5	0.004187	305.8	0.09322

Table (3.19) showed the values of lead concentration in seawater samples were lower than marine soil samples in table (3.20); this is due to the accumulation of lead metal in marine soils.

Table (3.21): Concentration of lead in seawater samples from Alahli Club (in front of Rear Gate of Benghazi University) (A), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
A_1	0.002806	193.6	0.09551
A_2	0.002669	182.2	0.09344
A_3	0.002278	149.8	0.08928
A_4	0.003001	209.6	0.09334
A_5	0.002696	183.8	0.09346

Table (3.22): Concentration of lead in marine soil samples from Alahli Club (in front of Rear Gate of Benghazi University) (A), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
A'_1	0.006046	454.4	0.07913
A'_2	0.006248	471.2	0.07234
A'_3	0.006166	464.4	0.07451
A'_4	0.006103	459.2	0.07652
A'_5	0.006246	471.1	0.07274

Garyounis is a populated area and traffic congestion due to cars and trucks, for this reason we find levels of lead is the highest. So, we found results of salinity, conductivity and total dissolved oxygen in Garyounis area were highest.

Lead pollution arises mainly from car exhausts but industrial processes, batteries, minerals and lead arsenate insecticide also contribute to lead in the environment (Timbrell, 2002).

Table (3.23): Concentration of lead in seawater samples from Nairoaz coast (N), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
N_1	0.001996	126.4	0.08991
N_2	0.002796	192.8	0.09812
N_3	0.002618	178.0	0.09876
N_4	0.002153	139.4	0.09334
N_5	0.002356	159.2	0.09397

Table (3.24): Concentration of lead in marine soil samples from Nairoaz coast (N), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
N'_1	0.005326	394.6	0.08055
N'_2	0.005182	382.5	0.08321
N'_3	0.005267	389.6	0.08665
N'_4	0.004903	359.3	0.08452
N'_5	0.005170	381.5	0.08631

Values of lead concentration in seawater samples were lower than marine soil samples; lead content in this area was attributed to the flow of sewage water from many places like the Tourist Village beach, the fertilizer factory and agricultural activities around Quarsha area which then flow to the seawater.

Table (3.25): Concentration of lead in seawater samples from Abou-Fakhra coast (K), (n=4), at 25˚C, using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
K_1	0.002180	141.7	0.09212
K_2	0.001830	112.7	0.09112
K_3	0.002298	151.5	0.08898
K_4	0.002245	147.1	0.09112
K_5	0.002003	138.2	0.09441

Table (3.26): Concentration of lead in marine soil samples from Abou-Fakhra coast (K), (n=4), at 25˚C, using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
K'_1	0.006128	461.2	0.07944
K'_2	0.005720	427.3	0.07453
K'_3	0.005886	441.1	0.07651
K'_4	0.005989	449.7	0.07651
K'_5	0.005726	427.7	0.07541

Table (3.25) showed the values of lead concentration in seawater samples were lower than marine soil samples in table (3.26).

Lead content at this area (K) was attributed to sewage discharge from the public who use this coast. It is known that coastal cities and residential areas near the beaches usually through their sewage and residues into the sea (after partial treatment or without treatment). Therefore, they would be polluted heavily with different kinds of pollutants, like domestic residues and other exhausted material available at roads and automobile waste of oil and fuels.

This in addition to other residues from small factories and other human activities, all of these pollutants contain element Lead. This metal great threat to all living being in the sea and on land.

Table (3.27): Concentration of lead in seawater samples from Geminis coast (I), (n=4), at 25˚C, using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
I_1	0.001125	114.3	0.05059
I_2	0.001201	115.5	0.05124
I_3	0.001076	105.9	0.05112
I_4	0.001252	119.4	0.04899
I_5	0.001213	116.4	0.05081

Table (3.28): Concentration of lead in marine soil samples from Geminis coast (I), (n=4), at 25˚C, using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
I'_1	0.004255	313.8	0.09096
I'_2	0.004428	328.1	0.09456
I'_3	0.004165	306.3	0.09341
I'_4	0.003821	277.8	0.09231
I'_5	0.004260	312.3	0.09541

Although this place is not very crowded, but the lead content was high in this area (I), this is due to the same reasons mentioned above which are mainly the sewage water which flow into the sea. As this area are known to be farming area, so most pollutants are mainly agricultural type including insecticide and pesticide and some fertilizers.

Table (3.29): The mean concentrations of lead in seawater and marine soil samples from Benghazi city coast using Atomic Absorption Spectroscopy:

Symbol	**Lead concentration ppb**	
	seawater	**Marine soil**
P	72.26	390.7
R	52.27	311.8
M	144.00	432.4
G	93.39	255.0
S	89.29	306.0
A	**183.80**	454.4
N	159.20	394.6
K	138.20	**461.2**
I	114.30	313.8

Showed the values of lead concentrations in seawater samples were lower than marine soil samples. Many marine crustaceans have been shown to accumulate metals (Coughlan et al, 1986). Garyounis is a populated area and traffic congestion due to cars and trucks. The amount of air pollution caused by metal has increased considerably due to industrial and car emission (Puchades et al, 1989).

Lead content at this area Abou-Fakhra coast (K) was attributed to sewage discharge from the public who use this coast. It is known that coastal cities and residential areas near the beaches usually through their sewage and residues into the sea (after partial treatment or without treatment). Metals have many sources from which they can flow into the seawater body, the most obvious inputs of material to the sea are through pipes discharging directly into it (Clark, 2001).

Lead pollution arises mainly from car exhausts but industrial processes, batteries, minerals and lead arsenate insecticide also contribute to lead in the environment (Timbrell, 2002)

3.4.2. Determination of cadmium:

Results of the analysis for seawater and marine soil samples taken from different places were shown in the following tables;

Table (3.30): Concentration of cadmium in seawater samples from Benghazi City Coast beside North Benghazi Power Station (P), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
P_1	0.001440	3.662	0.002985
P_2	0.001334	4.810	0.002645
P_3	0.001742	7.273	0.002564
P_4	0.001525	5.960	0.002765
P_5	0.001251	5.426	0.002941

Table (3.31): Concentration of cadmium in marine soil samples from Benghazi City Coast beside North Benghazi Power Station (P), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
P'_1	0.007397	41.62	0.003167
P'_2	0.007457	41.99	0.003231
P'_3	0.007424	41.79	0.003661
P'_4	0.007663	43.25	0.003262
P'_5	0.007532	42.16	0.003288

Table (3.30) showed the values of cadmium concentration in seawater samples were lower than marine soil samples in table (3.31); This is due to the accumulation of cadmium metal in soil.

Table (3.32): Concentration of cadmium in seawater samples from Ras-Almaingar Coast (R), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
R_1	0.001539	6.045	0.004180
R_2	0.001907	8.269	0.004223
R_3	0.001539	6.045	0.004180
R_4	0.001822	7.157	0.004110
R_5	0.001767	6.879	0.004231

Table (3.33): Concentration of cadmium in marine soil samples from Ras-Almaingar Coast (R), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
R'_1	0.009558	54.89	0.003016
R'_2	0.010211	66.12	0.003112
R'_3	0.009589	55.11	0.003441
R'_4	0.009638	58.87	0.003619
R'_5	0.009599	56.01	0.003341

Table (3.32) showed the values of cadmium concentration in seawater samples were lower than marine soil samples in table (3.33); this is due to the high density of cadmium metal. Cadmium content in this area (R) was attributed to oil spill and flow of the sewage water from the residential area at the Breaga oil company.

Table (3.34): Concentration of cadmium in seawater samples from near Seaport in front of Higher Court (M), (n=4), using FAAS.

Symbol	Flame Atomic Absorption Spectroscopy		
	Absorption	**Conc. (µg/l)**	**±SEM**
M_1	0.000980	2.673	0.003345
M_2	0.001297	4.585	0.003116
M_3	0.000754	1.307	0.003722
M_4	0.000637	0.601	0.003664
M_5	0.000839	2.291	0.003838

Table (3.35): Concentration of cadmium in marine soil samples from near Seaport in front of Higher Court (M), (n=4), using FAAS.

Symbol	Flame Atomic Absorption Spectroscopy		
	Absorption	**Conc. (µg/kg)**	**±SEM**
M'_1	0.009558	54.84	0.003016
M'_2	0.009871	56.75	0.003241
M'_3	0.009907	56.97	0.003112
M'_4	0.009886	56.85	0.003327
M'_5	0.009816	56.35	0.003821

Table (3.34) showed the values of cadmium concentration in seawater samples were lower than marine soil samples in table (3.35); this is due to the accumulation of cadmium metal in soil.

Table (3.36): Concentration of cadmium in seawater samples from Giliana Coast (G), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
G_1	0.000697	0.961	0.003563
G_2	0.000522	0.910	0.002998
G_3	0.000705	1.012	0.003841
G_4	0.000579	0.931	0.003443
G_5	0.000720	1.096	0.003834

Table (3.37): Concentration of cadmium in marine soil samples from Giliana Coast (G), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
G'_1	0.01184	68.85	0.002944
G'_2	0.01100	63.69	0.002851
G'_3	0.01099	63.62	0.002561
G'_4	0.01118	64.78	0.002676
G'_5	0.01221	65.24	0.002562

Table (3.38): Concentration of cadmium in seawater samples from Eshbilia (Soldiery Resort) coast (S), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
S_1	0.001367	5.006	0.003477
S_2	0.001969	8.648	0.003443
S_3	0.001283	4.500	0.003234
S_4	0.001394	5.171	0.003456
S_5	0.001473	5.831	0.003764

Table (3.39): Concentration of cadmium in marine soil samples from Eshbilia (Soldiery Resort) coast (S), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
S'_1	0.007667	43.62	0.003167
S'_2	0.008001	53.32	0.003221
S'_3	0.007468	41.21	0.003001
S'_4	0.007689	44.33	0.003359
S'_5	0.007893	45.86	0.003112

Table (3.38) showed the values of cadmium concentration in seawater samples were lower than marine soil samples in table (3.39); this is due to the accumulation of cadmium metal in marine soils.

Table (3.40): Concentration of cadmium in seawater samples from Alahli Club (in front of Rear Gate of Benghazi University) (A), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
A_1	0.001192	3.948	0.003117
A_2	0.001322	4.736	0.003456
A_3	0.001492	5.764	0.003755
A_4	0.001836	7.841	0.003811
A_5	0.001511	5.572	0.003769

Table (3.41): Concentration of cadmium in marine soil samples from Alahli Club (in front of Rear Gate of Benghazi University) (A), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
A'_1	0.006165	34.11	0.003279
A'_2	0.005772	31.72	0.003421
A'_3	0.005944	32.76	0.003456
A'_4	0.006489	36.09	0.003241
A'_5	0.006001	33.67	0.003831

Table (3.42): Concentration of cadmium in seawater samples from Nairoaz coast (N), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
$\mathbf{N_1}$	0.001159	3.752	0.003989
$\mathbf{N_2}$	0.001162	3.766	0.004378
$\mathbf{N_3}$	0.001610	6.477	0.004512
$\mathbf{N_4}$	0.001076	3.246	0.004110
$\mathbf{N_5}$	0.001321	4.310	0.004310

Table (3.43): Concentration of cadmium in marine soil samples from Nairoaz coast (N), (n=4), using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
$\mathbf{N'_1}$	0.008379	47.62	0.003136
$\mathbf{N'_2}$	0.008268	46.94	0.003211
$\mathbf{N'_3}$	0.008004	45.33	0.003167
$\mathbf{N'_4}$	0.008019	45.42	0.003421
$\mathbf{N'_5}$	0.008299	46.33	0.003118

Values of cadmium concentration in seawater samples were lower than marine soil samples, cadmium content in this area was attributed to the flow of sewage water from many places like the Tourist Village beach.

Table (3.44): Concentration of cadmium in seawater samples from Abou-Fakhra coast (K), (n=4), at 25˚C, using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (μg/l)**	**±SEM**
K_1	0.002515	11.950	0.002813
K_2	0.001807	7.666	0.003211
K_3	0.002167	9.846	0.003112
K_4	0.001370	2.809	0.003351
K_5	0.001997	8.067	0.003321

Table (3.45): Concentration of cadmium in marine soil samples from Abou-Fakhra coast (K), (n=4), at 25˚C, using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (μg/kg)**	**±SEM**
K'_1	0.009891	56.88	0.003015
K'_2	0.009842	56.58	0.003411
K'_3	0.009910	56.99	0.003751
K'_4	0.009682	55.60	0.003211
K'_5	0.009841	56.51	0.003287

Table (3.44) showed the values of cadmium concentration in seawater samples were lower than marine soil samples in table (3.45).

Cadmium content at this area (K) was attributed to sewage discharge from the public who use this coast. It is known that coastal cities and residential areas near the beaches usually through their sewage and residues into the sea (after partial treatment or without treatment). Therefore, they would be polluted heavily with different kinds of pollutants, like domestic residues and other exhausted material available at roads and automobile waste of oil and fuels. This in addition to other residues from small factories and other human activities in this area, all of these pollutants contain element cadmium. This metal great threat to all living being in the sea and on land.

Table (3.46): Concentration of cadmium in seawater samples from Geminis coast (I), (n=4), at 25˚C, using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/l)**	**±SEM**
I_1	0.001953	8.549	0.003523
I_2	0.002204	10.070	0.003606
I_3	0.001814	7.710	0.003281
I_4	0.002247	10.320	0.003456
I_5	0.002019	9.162	0.003696

Table (3.47): Concentration of cadmium in marine soil samples from Geminis coast (I), (n=4), at 25˚C, using FAAS.

Symbol	**Flame Atomic Absorption Spectroscopy**		
	Absorption	**Conc. (µg/kg)**	**±SEM**
I'_1	0.008872	93.40	0.005116
I'_2	0.009012	95.51	0.005441
I'_3	0.008488	88.95	0.005331
I'_4	0.00919	96.51	0.005112
I'_5	0.00903	95.39	0.005111

Although this place is not very crowded, but the lead content was high in this area (I), this is due to the same reasons mentioned above which are mainly the sewage water which flow into the sea. As this area are known to be farming area, so most pollutants are mainly agricultural type including insecticide and pesticide and some fertilizers.

Table (3.48): Comparison of the results obtained for analysis of cadmium and lead in different places using FAAS:

Symbol	**Cadmium concentration ppb**		**Lead concentration ppb**	
	Seawater	**Marine soil**	**seawater**	**Marine soil**
P	5.426	41.62	72.26	390.7
R	7.157	54.89	52.27	311.8
M	2.291	54.84	144.00	432.4
G	2.496	68.85	93.39	255.0
S	5.831	43.62	89.29	306.0
A	5.572	34.11	**183.80**	454.4
N	4.310	46.94	159.20	394.6
K	8.067	56.58	138.20	**461.2**
I	**9.162**	**93.40**	114.30	313.8

From the last comparison table for the Pb showed that marine soil is clear of lead but seawater is the higher of the allowed limit according to the Libyan standard specification due to exhausted material available at roads and automobile waste of oil , fuels and litters, as well as to other residues from small factories and other human activities in this area, sewage discharge pipes. Cadmium its clear both samples of seawater and marine soil.

Lead pollution arises mainly from car exhausts but industrial processes, batteries, minerals and lead arsenate insecticide also contribute to lead in the environment (Timbrell, 2002). The solubility of cadmium in water is influenced to a large degree by the acidity of the medium (Fleischer, 1974).

Conclusion:

In this research, we measured the trace amounts of lead and cadmium after preconcentration of the samples from the coast of Benghazi.

The preconcentration of trace amounts of lead and cadmium for using Atomic Absorption Spectrometer by a solvent extraction Dithizone complex was formed at pH 7-9.

The maximum extraction time was found to be 30 minutes, the lead-Dithizone complex shows maximum absorbance at 283.3nm; and the Cadmium-Dithizone complex shows maximum absorbance at 228.8 nm.

Lead in the seawater and from the results obtained in this study, notes that the highest concentration in the Alahli Club (in front of Rear Gate of Benghazi University) site and less focus on the Ras-Almaingar site, the sites of Geminis, Abou Fakhra, Nairoaz and near seaport front of Higher Court are almost equal.

All results obtained for lead in seawater was the highest of the allowed limit according to the Libyan standard specification which is 50 ppb and the American standard specification which is 15 ppb (Kegley et al, 1998).

Compared with the results were obtained in the previous study for the year 2007, the results of this study for concentration of lead is higher than the previous study, because of the increase horrible in the number of motor vehicles, frequent use weapons and the use of explosives TNT dramatically, all cause air pollution then into the seawater.

For the sands of the sea were the highest concentration at the site of Abou Fakhra and less concentration of lead in Giliana, the sites Geminis, Nairoaz, beside North Benghazi Power Station, Ras-Almaingar and Eshbilia are almost equal.

There for is no Libyan standard specification for soil, but according to the international standard measurements for quality of soil for Lead in China is ≤ 35 mg/kg,(Daoji et al, 2004) and in Sweden is less than 10 ppm (Daoji et al, 2004). So, all results were obtained do not exceed the allowed limit according to the quality of soil in China and Sweden.

Compared with the results were obtained in the previous study, the lead levels greater than the results were obtained in this study and cause is, all sewage discharge pipes blocked along the coast of the city of Benghazi.

(I) (II)

Figure (4.1): (I) Discharge wastes slaughter on In front of Real Gate of Benghazi University; (II) Discharge wastes slaughter on Al-Sabri beach.

The concentration of ***cadmium*** in seawater in Benghazi was in the site of Geminis contains the highest concentration while less focus near Seaport in front of Higher Court.

Beside North Benghazi Power Station, Eshbilia and the Alahli Club (In front of Real Gate of Benghazi University) are nearly equal, also near seaport front of Higher Court and Giliana are almost equal. The standard measurements for quality of seawater for cadmium in China is 10 ppb.

So, all results were obtained do not exceed the allowed limit according to the quality of seawater in China. The concentration of cadmium in the sands of the sea were the highest concentration at the site of Geminis and less concentration at the site of the Alahli Club (In front of Real Gate of Benghazi University).

Concentration of cadmium in the sites Abou Fakhra, near seaport front of Higher Court and Ras-Almaingar are almost equal and Eshbilia, beside North Benghazi Power Station and Nairoaz are almost equal.

The concentration of Cd in soils of Japan is 450 ppb on average (N. Herawati et al, 1981). So, all results obtained do not exceed the allowed limit according to the quality of soil in Japan. Standard measurements for quality of soil for cadmium in China is ≤ 200 ppb. So, all results was obtained do not exceed the allowed limit according to the quality of soil in China.

Chapter(5) Appendixes:

Statistical Analysis of the Results Obtained Using Atomic Absorption Spectroscopy:

Appendix section 1. Lead in seawater samples**:**

Concentrations of Lead in seawater samples ppb					
symbol	P	R	M	G	S
X_1	51.72	61.21	139.0	83.66	94.83
X_2	88.71	53.30	158.6	101.5	82.07
X_3	68.80	58.81	139.4	102.5	81.24
X_4	79.83	55.67	138.8	85.91	99.02
X_5	72.26	52.27	144.0	93.39	89.29
Mean	**72.26**	**56.25**	**143.9**	**93.39**	**89.29**
±SEM	**0.05175**	**0.04330**	**0.04980**	**0.05116**	**0.05128**
SD	**0.01594**	**0.02631**	**0.009776**	**0.009987**	**0.008988**
RSD%	**22.05**	**14.42**	**6.790**	**10.69**	**10.07**

Concentrations of Lead in seawater samples ppb				
symbol	A	N	K	I
X_1	193.6	126.4	141.7	116.4
X_2	182.2	192.8	112.7	115.5
X_3	149.8	178.0	151.5	105.9
X_4	209.6	139.4	147.1	119.4
X_5	183.8	159.2	138.2	114.3
Mean	**183.8**	**159.1**	**138.2**	**114.3**
±SEM	**0.09346**	**0.09397**	**0.09441**	**0.05059**
SD	**0.02538**	**0.03137**	**0.01751**	**0.005849**
RSD%	**13.81**	**19.71**	**12.67**	**5.119**

Appendix section 2. Lead in marine soil samples**:**

Concentrations of Lead in marine soil samples ppb					
symbol	P′	R′	M′	G′	S′
X_1	390.7	311.8	432.4	255.0	306.0
X_2	394.4	294.0	423.8	241.6	286.4
X_3	397.8	268.6	469.2	243.7	309.3
X_4	368.8	326.2	440.3	253.3	321.7
X_5	387.9	300.1	441.4	248.4	305.8
Mean	**387.9**	**300.1**	**441.4**	**248.4**	**305.8**
±SEM	**0.08934**	**0.09109**	**0.08829**	**0.09262**	**0.09097**
SD	**0.01309**	**0.02482**	**0.01969**	**0.04488**	**0.01463**
RSD%	**3.375**	**8.271**	**4.460**	**19.98**	**4.784**

Concentrations of Lead in seawater samples ppb				
symbol	A′	N′	K′	I′
X_1	454.4	394.6	461.2	313.8
X_2	471.2	382.5	427.3	328.1
X_3	464.4	389.6	441.1	306.3
X_4	459.2	359.3	449.7	277.8
X_5	462.3	381.5	444.8	306.5
Mean	**462.3**	**381.5**	**444.8**	**306.5**
±SEM	**0.07913**	**0.08055**	**0.07944**	**0.09096**
SD	**0.007197**	**0.01559**	**0.01423**	**0.02116**
RSD%	**1.557**	**4.087**	**3.218**	**6.903**

Appendix section 3. Cadmium in seawater samples:

Concentrations of Cadmium in seawater samples ppb					
symbol	P	R	M	G	S
X_1	3.662	6.045	2.673	0.961	5.006
X_2	4.810	8.269	4.585	0.910	8.648
X_3	7.273	6.045	1.307	1.012	4.500
X_4	5.960	7.157	1.601	0.931	5.171
X_5	5.426	6.879	2.291	0.953	5.831
Mean	**5.426**	**6.88**	**2.491**	**0.953**	**5.831**
±SEM	**0.002985**	**0.003022**	**0.003838**	**0.003834**	**0.003764**
SD	**0.002074**	**0.003216**	**0.001835**	**0.004670**	**0.001899**
RSD%	**3.461**	**5.774**	**2.605**	**1.158**	**2.297**

Concentrations of Cadmium in seawater samples ppb				
symbol	A	N	K	I
X_1	3.948	3.752	11.950	8.549
X_2	4.736	3.766	7.666	10.070
X_3	5.764	6.477	9.846	7.710
X_4	7.841	3.246	2.809	10.320
X_5	5.572	4.310	8.067	9.162
Mean	**5.572**	**4.310**	**8.068**	**9.162**
±SEM	**0.003769**	**0.004310**	**0.003321**	**0.003696**
SD	**0.001685**	**0.001464**	**0.002629**	**0.001245**
RSD%	**30.24**	**33.98**	**8.352**	**13.59**

Appendix section 4. Cadmium in marine soil samples:

Concentrations of Cadmium in marine soil samples ppb					
symbol	P′	R′	M′	G′	S′
X_1	41.99	54.89	54.84	68.85	43.62
X_2	41.62	66.12	56.75	63.69	53.32
X_3	41.79	55.11	56.97	63.62	41.21
X_4	43.25	58.87	56.85	64.78	44.33
X_5	42.16	56.01	56.35	65.24	45.86
Mean	**42.162**	**58.200**	**56.352**	**65.236**	**45.668**
±SEM	**0.003167**	**0.003305**	**0.003016**	**0.002944**	**0.003172**
SD	**0.000739**	**0.004735**	**0.001014**	**0.002470**	**0.004591**
RSD%	**1.755**	**1.888**	**1.800**	**3.786**	**1.771**

Concentrations of Cadmium in seawater samples ppb				
symbol	A′	N′	K′	I′
X_1	34.11	47.62	56.88	93.40
X_2	31.72	46.94	56.58	95.51
X_3	32.76	45.33	56.99	88.95
X_4	36.09	45.42	55.60	96.51
X_5	33.67	46.33	56.51	95.39
Mean	**33.67**	**46.33**	**56.51**	**93.952**
±SEM	**0.003279**	**0.003118**	**0.003015**	**0.005222**
SD	**0.001885**	**0.001136**	**0.000634**	**0.003014**
RSD%	**5.598**	**2.451**	**1.122**	**3.771**

Appendix section 5. The physical properties of Lead:

Physical properties of lead	
Atomic number	82
Atomic mass	207.2 g.mol^{-1}
Electronegativity according to Pauling	1.8
Density	11.34 g.cm^{-3} at 20°C
Melting point	327 °C
Boiling point	1755 °C
Vanderwaals radius	0.154 nm
Electronic shell	[Xe] 4f^{14} 5d^{10} 6s$^{2\ 6p2}$
Isotopes	13
Ionic radius	0.132 nm (+2) ; 0.084 nm (+4)
Energy of first ionization	715.4 kJ.mol^{-1}
Energy of second ionization	1450.0 kJ.mol^{-1}
Energy of third ionization	3080.7 kJ.mol^{-1}
Energy of fourth ionization	4082.3 kJ.mol^{-1}
Energy of fifth ionization	6608 kJ.mol^{-1}
Discovered by	The ancients

Appendix section 6. The physical properties of cadmium:

Physical properties of Cd	
Atomic number	48
Atomic mass	112.4 g.mol^{-1}
Electronegativity according to Pauling	1.7
Density	8.7 g.cm^{-3} at 20°C
Melting point	321 °C
Boiling point	767 °C
Vanderwaals radius	0.154 nm
Ionic radius	0.097 nm (+2)
Isotopes	15
Electronic shell	[Kr] 4d^{10} 5s^{2}
Energy of first ionization	866 kJ.mol^{-1}
Energy of second ionization	1622 kJ.mol^{-1}
Standard potential	-0.402 V
Discovered	Fredrich Stromeyer in 1817

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جامعة بنغازي

كلية العلوم

قسم الكيمياء

تقدير الرصاص و الكادميوم في ساحل مدينة بنغازي باستخدام مطياف الامتصاص الذري

لإكمال متطلبات الحصول علي الإجازة العليا

{الماجستير}

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2013 م

الخلاصة :

في هذا البحث، قمنا بقياس الكميات الضئيلة من الرصاص و الكادميوم بعد معالجة العينات التي تم جمعها من ساحل مدينة بنغازي.

معالجة الكميات الضئيلة من الرصاص و الكادميوم تتم لاستخدام مطياف الامتصاص الذري وذلك بواسطة الاستخلاص بالمذيب باستخدام Dithizone عند درجة الحموضة من 7- 9.

عند زمن استخلاص 30 دقيقة يعطي معقد (الرصاص- Dithizone) أعلي امتصاصية عند طول موجي 283.3 نانومتر، ومعقد (الكادميوم- Dithizone) عند طول موجي 228.8 نانومتر.

الرصاص في ماء البحر, من النتائج المتحصل عليها في هذه الدراسة نلاحظ أن أعلي تركيز في موقع نادي الأهلي مقابل جامعة بنغازي و أقل تركيز في موقع رأس المنقار, أما المواقع قمينس و ابوفاخرة و النيروز و بالقرب من ميناء بنغازي تكون تقريبا متساوية.

كل نتائج الرصاص المتحصل عليها في مياه البحر كانت أعلي من الحد المسموح بيه في الموصفات القياسية الليبية (50 ppb) و الأمريكية (15 ppb).

بالمقارنة مع النتائج المتحصل عليها في الدراسة السابقة لسنة 2007 م, كانت النتائج المتحصل عليها في هذه الدراسة أعلي في تركيز الرصاص من الدراسة السابقة بسبب الزيادة الرهيبة في عدد المركبات الآلية و كثرة استعمال الأسلحة النارية و متفجرات TNT بشكل كبير وكلها تسبب تلوث الهواء ومنه إلي الماء.

بالنسبة لرمال البحر كان أعلي تركيز للرصاص في موقع ابوفاخرة وأقل تركيز للرصاص في موقع جليانة و مواقع قمينس و النيروز و محطة شمال بنغازي و رأس المنقار و اشبيلية تكون تقريبا متساوية.

كل نتائج الرصاص المتحصل عليها في رمال البحر كانت ضمن الحد المسموح بيه في الموصفات القياسية الصينية و السويدية التي تكون اقل من (10 ppm).

وبالمقارنة مع النتائج المتحصل عليها في الدراسة السابقة (2007) فإن مستويات الرصاص أكبر من النتائج المتحصل عليها في هذه الدراسة (2012) و ذلك بسبب إيقاف جميع أنابيب الصرف الصحي الموجودة علي طول سواحل مدينة بنغازي.

شكل (1.4): أنبوب الصرف الصحي الموجود بمنطقة الصابري.

بالنسبة لتركيز الكادميوم في الساحل البحري لمدينة بنغازي, كان موقع قمينس يحوي أعلي تركيز بينما أقل تركيز بالقرب من ميناء بنغازي.

مواقع محطة شمال بنغازي و النيروز و نادي الأهلي مقابل جامعة بنغازي تقريبا متساوية و أيضا مواقع بالقرب من ميناء بنغازي و جليانة تقريبا متساوية.

كل نتائج الكادميوم المتحصل عليها في مياه البحر كانت أقل من الحد المسموح به في الموصفات الصينية (10 ppb).

تركيز الكادميوم في رمال البحر كان أعلي تركيز في موقع قمينس و أقل تركيز في موقع نادي الأهلي مقابل جامعة بنغازي.

تركيز الكادميوم في مواقع ابوفاخرة و ميناء بنغازي و رأس المنقار تقريبا متساوية, ومواقع اشبيلية و محطة الشمال و النيروز تقريبا متساوية.

كل نتائج الكادميوم المتحصل عليها في رمال البحر في هذا الدراسة كانت أقل من الحد المسموح به في الموصفات الصينية (≤ 200 ppb), وأيضا أقل من الحد المسموح بيه في الموصفات اليابانية (450 ppb).

لا توجد إي دراسة سابقة لقياس تركيز عنصر الكادميوم في مياه و رمال سواحل مدينة بنغازي لمقارنتها مع النتائج المتحصل عليها في هذه الدراسة.