# Direct Determination of Heavy Metal in Tanks Water in South of The Kingdom Of Saudi Arabia by Anodic Stripping Voltammetry Technique

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**Abstract:** In this work, the direct determination of some trace heavy metals in the tanks water were carried out by differential pulse anodic stripping voltammetry (DPASV) technique at Multi Mode Electrode (MME) ,mercury drop capillary for MME working electrode, using a differential pulse mode. The stripping current arising from the oxidation of metals were connected with the concentration the metals in the sample. The concentration of some trace heavy metals found in tanks water sample were determined using acetate buffer (pH: 4.2). This value of elements in this study is between the limit values suggested by WHO and EPA , it is understood that the concentration of Zn(II), Cu(II), Pb(II) and Cd(II) in tanks water of Abu-Arish, Sabia, Jazan and Bani-Malik areas have no influence on the human health.
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**Keywords:** tanks water; voltammetry; Saudi; trace elements.

## 1.Introduction

Groundwater quality was determined in Jazan city southwest of Saudi Arabia, groundwater samples were selected during July 2010 (dry season). Selections of metals which may be toxic in excess when present in drinking water were further discussed (As, Cd, pb, Cu, Cr, Hg, Mn, Ni, Zn, Fe, and Se). Quantitative identification and determination of Total Petroleum Hydrocarbon (TPH), Hydrocarbon C10-C40 (diesel hydrocarbon fraction), Volatile Organic Compounds (VOCs), Poly Aromatic Hydrocarbons (PAHs), Total Herbicides and Organochlorine Pesticides in samples based on applications of gas chromatograph (GC). The chemical analysis of groundwater samples show that all samples comply with WHO standards for the parameters measured. Overall the water quality is found to be suitable for drinking purposes without any prior treatment (Alshikh., 2011). The direct determination of some trace heavy metals in the tap water were carried out by voltammetry. This value of elements in this study is between the limit values suggested by WHO, it is understood that the concentration of Zn(II), Cu(II), Pb(II) and Cd(II) in Tap water of Abu-Arish, Sabia, Jazan and Bani-Malik areas have no influence on the human health (Arab and Alshikh., 2012) .In Jazan area south Kingdom of Saudi Arabia illustrates that the average daily water consumption of citizens did not exceed 115 liter/day. A 17% decrease in water consumption in comparison to 1415h. A periodic chemical analysis was also undertaken (over the last three years) in the MOMRA1, Tahliyah and ICE laboratories to determine the purity of the water in their tanks. No biological or organic impurities were found. However in comparison, the public water networks and tanks that were tested contained chronic organic biologic impurities. This was considered due to the use of the impure clay and heavy materials used to line the tanks. These materials caused sediment and sludge to build up and as a consequence block and close the network tubes from working effectively and efficiently, causing an economical and health problem for the citizens and the municipality. The study illustrates that 92% weight of sediment and sludge has a united reaction susceptibility with HCL (3M) acid. This in turn means a build-up of $CaCo^{3,}$ far exceeding the 2 micron molecule diameter normally encountered, This created a bigger qualitative surface inside the tanks and pipelines. The chemical structures were also analyzed using x-ray florescence spectrometry for non-organic complex molecules formed in the large vacuum voids. These structures may cause the growth of foci of a micro-biological nature and thus diminish the effects of the chlorine in the water and could cause a health problem (AL-bakri and Break, 2004).

## 2. Materials and methods

### Gathering samples:

Tanks water samples were chosen from The areas, Abu-Arish , Sabia, Jazan and Bani-Malik. Before water sampling, all the glass bottles were cleaned and rinsed thoroughly with water to be analyzed. All reagents used were of analytical grade. Samples were unfiltered and the concentration of the different parameters could correspond to the total

concentration of the tanks water elements was used by the consumers.

**The apparatus used in the study:**

The concentration of trace elements were measured by Polargraph instrumental 746 VA trace analyzer with 747 VA stand or from Metrohm company (Herisau, Switzerland) with a three-electrode system consisting of a WE Multi Mode Electrode (MME) ,Mercury drop capillary for MME working electrode, a platinum wire auxiliary electrode and Ag / AgCl (NaCl / 3M , Metrohm ) reference electrode figure 1. After the experimental parameters were recorded, the sample in the voltametric cell was sprayed with nitrogen for 300s. All pH measurements were made with Model Metrohm 744 pH meter (Herisau, Switzerland) at ambient temperature of the laboratory (25-30 °C). The information storage is done by a computer, from Toshiba company 757 VA computracy joined with the device.

**3. Results and Discussion**

Jazan region is one of the administrative regions of the Kingdom of Saudi Arabia is located in southern Saudi Arabia on the southern border with the Republic of Yemen, overlooking the Red Sea, there is the port of Jizan third ports of the Kingdom in terms of capacity and features diverse environmental and climate and is the gateway state Actual Islands Knights and the effects of dating to 8000 before of birth figure 1.


**Figure 1. Area of Jazan.**

The study has illustrated economical difficulties as a result of buying bottled drinking water. The chemical analysis results illustrate that the region's water is suitable given its main components (calcium - magnesium - sulphates - chlorides ) in terms of non-bottled drinking water (701-2000), except for the existence of some organic substances (which have a plant origin) and a tiny amount of sand. We have applied the relationships of the ionic balance based on a reasonable assumption for our studies, and calculated the error range percentage of these assumptions. The value error range which has been estimated is about 1.26%. It was noticed that the drinking water which is used, and where we have analyzed some of its main elements, plus counting the amount of its sodium content, has an amount of total dissolved salts (T.D.S) in the minimum or less than the minimum (100 milligram/liter). These results could have a negative effect on the citizen's health, with the increasing probability of salt deficiency in their bodies. In addition the higher temperatures and moisture content in the area obviously increases the sweat factor. We have calculated mathematically the range of the ionic balance and T.D.S of 12 samples of bottled water from different sources. When comparing them to percentages written on the bottles, it was noticed that the percentage of the different averages between cations and anions is between (0-27.54%). The percentages stated and those we calculated are at odds and thus a cause for concern. This has lead us to the conclusion that the apparatus used in standardizing need to be calibrated periodically if accurate figures are to be determined. It was further noticed from the results of the blood analyses of 101 samples that 16% (17% males and 12.7% females) from the group, whose ages are between 17-40 years, suffered from a lack of calcium in their blood, whereas 52% from that group suffered from calcium excess. Those marked as normal (32%), are between 2-2.6 milimole/litre (AL-Bakri and Break, 2004).

Electrochemical methods, first of all anodic stripping voltammetry (ASV), are still recognized as the most convenient techniques for measuring trace heavy metals. Namely, due to the capability of pre-concentrating analytes at/in the surface of the working electrode, ASV allows quantification of heavy metals down to a microgram or even nanogram per liter concentration level (Guzsvány *et al.,*2010). Stripping analysis has proved a useful and versatile technique for the determination of trace metals in various samples of environmental clinical and industrial origin (Demetriades *et al.,* 2004). Anodic stripping voltammetry (ASV) is an established method for trace metal ion analysis in contaminated water samples(Sonthalia *et al.,*2004). A simple, fast and sensitive method has been developed for environmental water analysis by using differential pulse stripping voltammetry (DPSV) performed on a hanging mercury drop electrode (HMDE)(Yi He *et al.,* 2007). In this research the estimation of Pb ,Cd , Cu , Zn , Fe, Se concentration in the tanks water of

Jizan in Kingdom Of Saudi Arabia city was accomplished using voltammetry techniques.

**I- Determination of Zinc (Zn) trace elements in Tanks water sample:**

In this study, the concentration of Zn trace element in tanks water was successfully determined by ASV technique. DPAS voltammograms of Zn element obtained from standard addition technique are given in Fig. 2. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation Fig.3. (Used voltammetric apparate on quantitative mode a automatically requires one sample to be added to the voltammetric cell and then two standards to be added and finally, the machine plots the value of the current- concentration. Therefore, there are only three plots on calibration curve). Consequently, linear calibration range was automatically obtained as being related to quantitative mode of the voltammetric unit.

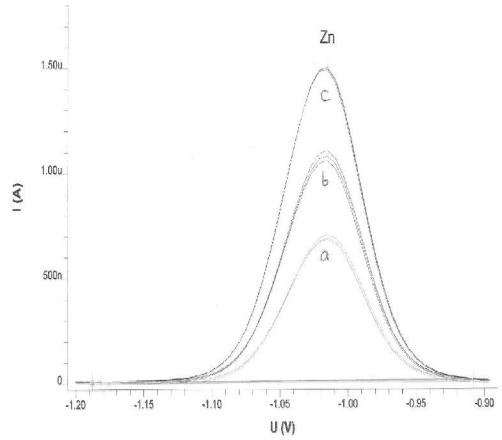


**Figure 2. DPAS voltamograms of the Zn element obtained from standart addition technique. a) 1 ml acetate buffer (pH = 4.2) + 10 ml Tanks water. b) a + 100 µl. c) b + 100 µl standart solution of Zn (10 mg /l).**

As can be seen from the Fig. 2, the current of oxidation peak of Zinc element increased by the addition of the standard solution. A further increase in sensitivity of peak currents was achieved by increasing the deposition time to 300 s. In addition , to increase sensitivity, the optimum pH value in acetate buffer tampon was determined to be 4.2. Under these conditions.

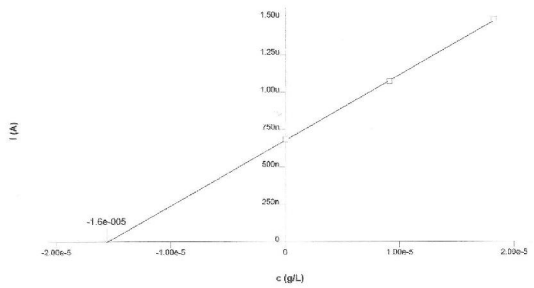


**Figure 3. The calibration plot of Zn (II) element obtained from standard addition by DPASV technique.**

Zinc (Zn) is environmentally ubiquitous and essential for life; one estimate suggests 20% of the world's population is at risk of Zn deficiency. Manifestations include abortion, teratology, prematurity, retarded growth and development, low immunity, poor healing, dermatitis, low physical work capacity, abnormal neuropsychological functions, and other abnormalities (Harold *et al.*,2007).

The study approved that the highest concentration of Zn element was found Bani - Malik area top tanks water which reached (0.61 mg/l) then Abu-Arish area tanks water reached to (0.32 mg/l) , then Sabia area tanks water reached to (0.286 mg/l) finally Jazan area tanks water reached to (0.21 mg/l), finally in figure 4.

As can be seen from the Fig. 4, that the highest concentration of Zn element was found Sabia area bottom tanks water which reached (0.571 mg/l) . While Jazan area bottom tanks water has the lower concentration it reached (0.114 mg/l).

This value is between the limit values suggested by WHO and EPA, it is understood that the concentration of Zn(II) in tanks water have no influence on the human health.

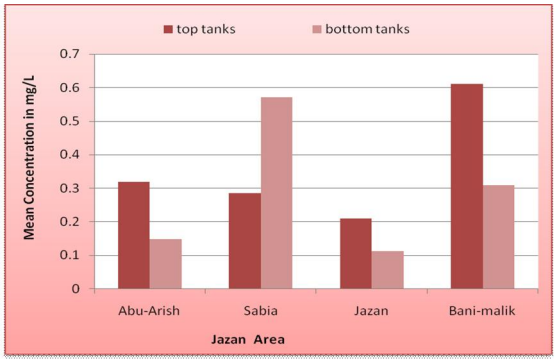


**Figure 4. Mean Concentrations of Zinc element in Jazan Area.**

**II- Determination of Lead (Pb) trace elements in tanks water sample:**

In this study, the concentration of Pb trace element in tanks water was successfully determined by ASV technique. DPAS voltammograms of Pb element obtained from standard addition technique are given in Fig 5. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation (Fig 6). (Used voltammetric apparate on quantitative mode a automatically requires one sample to be added to the voltammetric cell and then two standards to be added and finally, the machine plots the value of the current- concentration. Therefore, there are only three plots on calibration curve). Consequently, linear calibration range was automatically obtained as being related to quantitative mode of the voltammetric unit.

As can be seen from the Fig. 5, the current of oxidation peak of Lead element increased by the addition of the standard solution. A further increase in sensitivity of peak currents was achieved by increasing the deposition time to 300 s. In addition , to increase sensitivity, the optimum pH value in acetate buffer tampon was determined to be 4.2. Under these conditions.

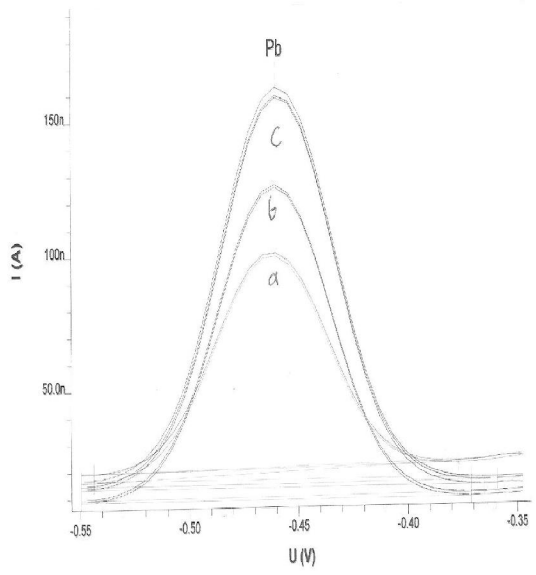


**Figure 5. DPAS voltamograms of the Pb element obtained from standart addition technique a) 1 ml acetate buffer (pH = 4.2) + 10 ml tanks water . b) a + 100 µl. c) b + 100 µl standart solution of Pb (10 mg /l).**

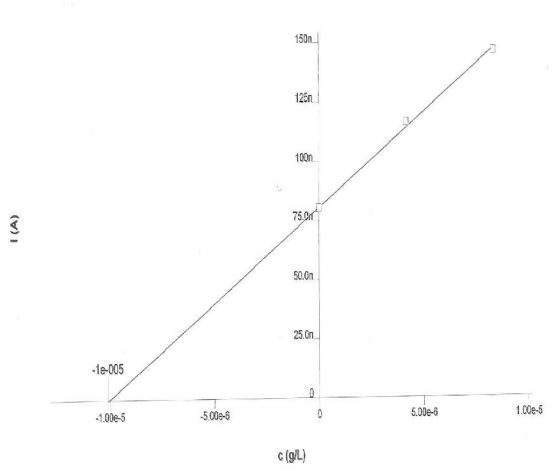


**Figure 6. The calibration plot of Pb (II) element obtained from standard addition by DPASV technique.**

Inorganic lead is certainly the most extensively studied of all toxic agents. Toxic effects may occur in the central and peripheral nervous systems, blood, kidney, and cardiovascular, endocrine and immune systems, gastrointestinal tract, and male reproduction. Lead causes increase of blood pressure, (Dragoe *et al.,* 2006, Skerfving and Bergdahl, 2007).

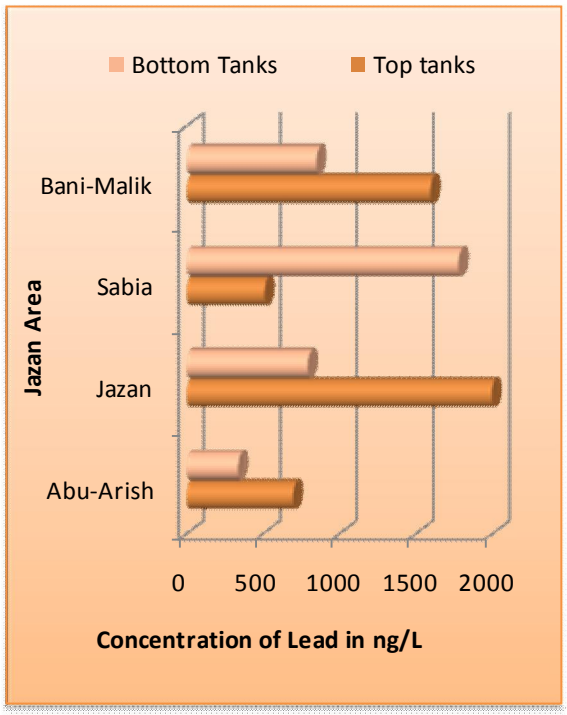


**Figure 7. Mean Concentrations of Lead element in Jazan Area.**

The highest concentration was found with Pb element noticed is (1999 ng/l) in Jazan area top tanks water , while Sabia area top tanks water has the lower concentration it reached (514.238 ng/l) the order is:

Sabia area bottom tanks water > Bani-Malik area bottom tanks water > Jazan area bottom tanks water > Abu-Arish area bottom tanks water figure 7.

This value is between the limit values suggested by WHO and EPA, it is understood that the concentration of Pb(II) in Tanks water have no influence on the human health.

**III- Determination of Copper (Cu) trace elements in tanks water sample:**

In this study, the concentration of Cu trace element in tanks water was successfully determined by ASV technique. DPAS voltammograms of Pb element obtained from standard addition technique are given in Fig 8. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation (Fig 9). (Used voltammetric apparate on quantitative mode a automatically requires one sample to be added to the voltammetric cell and then two standards to be added and finally, the machine plots the value of the current- concentration. Therefore, there are only three plots on calibration curve). Consequently, linear calibration range was automatically obtained as being related to quantitative mode of the voltammetric unit.

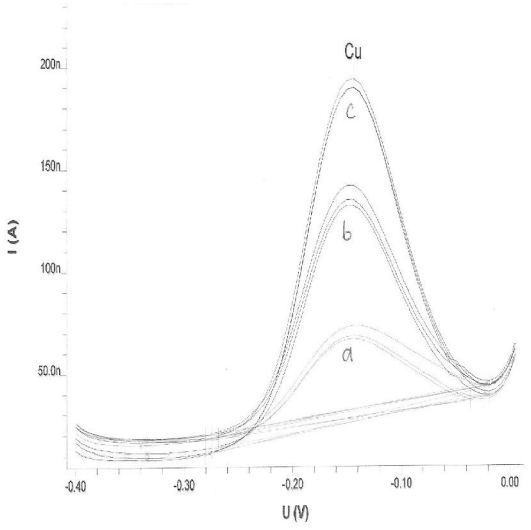


**Figure 8. DPAS voltamograms of the Cu element obtained from standard addition technique a) 1 ml acetate buffer (pH = 4.2) + 10 ml tanks water. b) a + 100 µl. c) b + 100 µl standart solution of Cu (10 mg /l).**

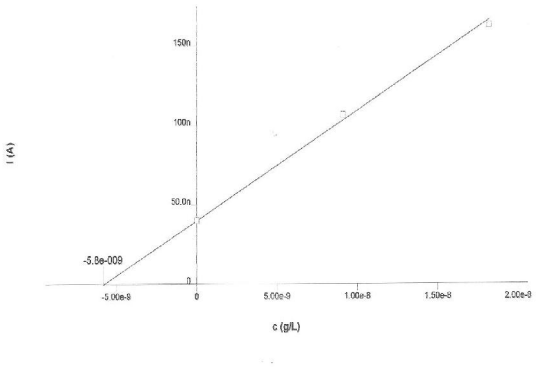


**Figure 9. The calibration plot of Cu (II) element obtained from standard addition by DPASV technique.**

As can be seen from the Fig. 8, the current of oxidation peak of Cu element increased by the addition of the standard solution. A further increase in sensitivity of peak currents was achieved by increasing the deposition time to 300 s. In addition , to increase sensitivity, the optimum pH value in acetate buffer was determined to be 4.2. Under these conditions.

Copper is a vital and toxic for many biological systems, so that its determination in water samples is warranted by the narrow window of concentration between essentiality and toxicity. It can be easily released from silicates, sulfites and oxides after some physical and chemical weathering and then transferred by water into soil and sediments (Faraji *et al.*,2009).

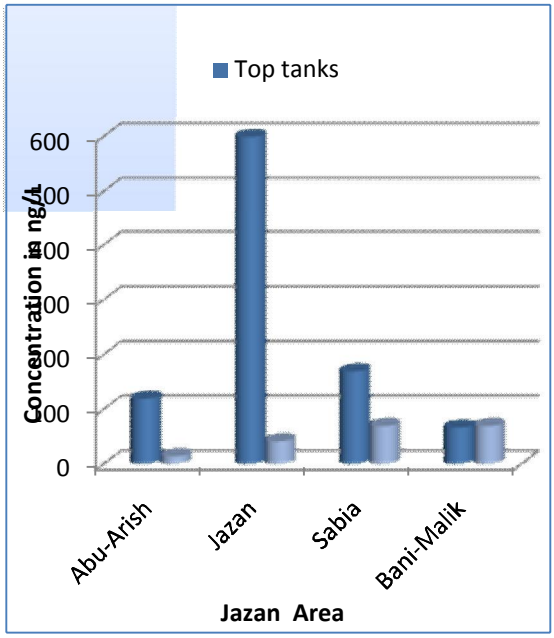


**Figure 10. Mean Concentrations of Copper element in Jazan Area.**

Also the study showed that the highest concentration Cu element was in Jazan area top tanks water (600 ng/l) then Sabia area top tanks water where (170 ng/l), then Abu-Arish area area top tanks water (120.2 ng/l) then Bani-Malik area top tanks water (67.3 ng/l) figure 10.

That the highest concentration of Cu element was found Bani-Malik area bottom tanks water which reached (70.3 ng/l) . While Abu-Arish area bottom tanks water has the lower concentration it reached (15.2ng/l).

This value is between the limit values suggested by WHO and EPA, it is understood that the concentration of Cu(II) in Tanks water have no influence on the human health.

**IV- Determination of Cadmium (Cd) trace elements in tanks water sample:**

In this study, the concentration of Cd trace element in tanks water was successfully determined by ASV technique. DPAS voltammograms of Cd element obtained from standard addition technique are given in Fig 11. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation (Fig. 12). (Used voltammetric apparate on quantitative mode a automatically requires one sample to be added to the voltammetric cell and then two standards to be added and finally, the machine plots the value of the current- concentration. Therefore, there are only three plots on calibration curve). Consequently, linear calibration range was automatically obtained as being related to quantitative mode of the voltammetric unit.

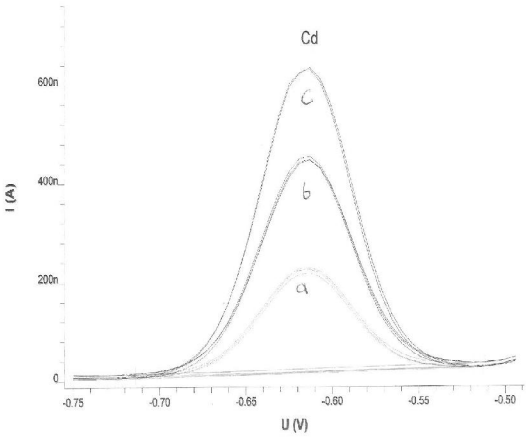


**Figure 11. DPAS voltamograms of the Cd element obtained from standard addition technique a) 1 ml acetate buffer (pH = 4.2) + 10 ml tanks water. b) a + 100 µl. c) b + 100 µl standard solution of Cd (10 mg /l).**

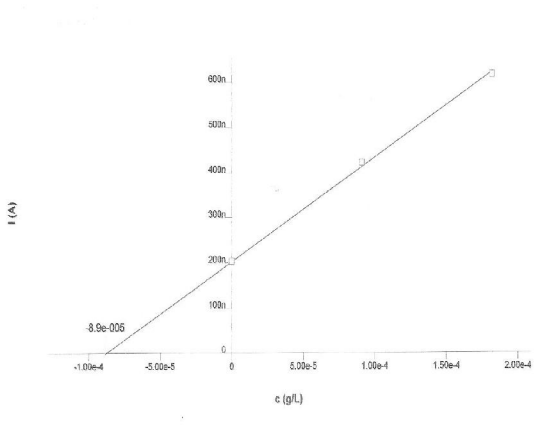


**Figure 12. The calibration plot of Cd (II) element obtained from standard addition by DPASV technique.**

As can be seen from the Fig. 11, the current of oxidation peak of Cd element increased by the addition of the standard solution. A further increase in sensitivity of peak currents was achieved by increasing the deposition time to 300 s. In addition , to increase sensitivity, the optimum pH value in acetate buffer was determined to be 4.2. Under these conditions.

Cadmium is a toxic and carcinogenic metal. The primary sources of cadmium exposure are cigarette smoke, food intake (shellfish, offal and certain vegetables), and ambient air, particularly in urban areas and in the vicinity of industrial settings, (Zhang *et al.,*2009).

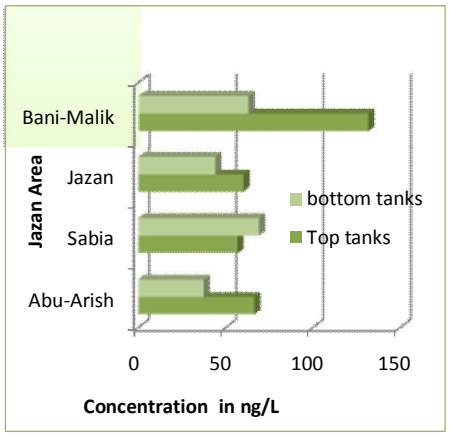


**Figure 13. Mean Concentrations of Cadmium element in Jazan Area.**

Also the study showed that the highest concentration Cd element was in Bani-Malik area top tanks water (131.8 ng/l) then Abu-Arish area top

tanks water where (66 ng/l), then Jazan area top tanks water(60.2 ng/l) then Sabia area top tanks water (56.97 ng/l) figure 13.

That the highest concentration of Cd element was found Sabia area bottom tanks water which reached (69.148 ng/l) . While Abu-Arish area bottom tanks water has the lower concentration it reached (37.547ng/l).

This value is between the limit values suggested by WHO and EPA, it is understood that the concentration of Cd(II) in tanks water have no influence on the human health .

Also the study clarified the differences between elements concentration, so that it can be seen in:

1. ***Jazan area Tanks water*** , the highest concentration Zn element is found, that it reached to (0.21 mg/l) in top tanks water where the less concentration was Cu element , that it reached to (42.3 ng/l) in bottom tanks water . Pb element reached to (796.8 ng/l) in bottom tanks water , following that ,Cd element where it reached (44.24 ng/L) in bottom tanks water (Table 1).
2. ***Abo - Arish area Tanks water:*** Concentration of Cu element, it was the lowest concentration within (15.2 ng/l) in bottom tanks water following that Cd element within (37.547 ng/l) in bottom tanks water after that Pb element within (700.4 ng/l) in top tanks water and the highest concentration was Zn element within (0.32 mg/l) in top tanks water table 1.
3. ***Sabia area Tanks water*:** in that the highest concentration Zn element was within (0.571 mg/l) in bottom tanks water , and it was lower in concentration Cd element within (56.97 ng/l) in top tanks water , and Pb element concentration reached to (514.238 ng/l in top tanks water while Cu element concentration reached to ( 170 ng/l ) in top tanks water (Table 1).
4. ***Bani-Malik area Tanks water*** Concentration of Pb element within (853 ng/l) in bottom tanks and Cu element concentration reached to (70.3 ng/l) in bottom tanks while the lowest concentration was in Cd element where it reached to (63.1 ng/l) in bottom tanks and the highest concentration was Zn element within (0.61 mg/l) in top tanks (Table 1).

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**Table 1: Concentration of heavy metal in Jazan Area.**

| Concentration of heavy metal | | | | | |
|---|---|---|---|---|---|
| Area | Tanks | Zn in mg/L | Cd in ng/L | Pb in ng/L | Cu in ng/L |
| Jazan | Top | 0.21 | 60.2 | 1999 | 600 |
| | Bottom | 0.114 | 44.24 | 796.8 | 42.3 |
| Abu-Arish | Top | 0.32 | 66.5 | 700.4 | 120.2 |
| | Bottom | 0.148 | 37.547 | 341.7 | 15.2 |
| Sabia | Top | 0.286 | 56.97 | 514,238 | 170 |
| | Bottom | 0.571 | 69.148 | 1781.91 | 70.2 |
| Bani-Malik | Top | 0.61 | 131.8 | 1598.8 | 67.3 |
| | Bottom | 0.31 | 63.1 | 853 | 70.3 |

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