

Heavy Metal Concentrations of Drinking Water in South of the Kingdom of Saudi Arabia

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Abstract: Drinking water is an important factor in survival. Many trace elements, both metals and non-metals, in drinking water are capable of causing human diseases if their concentrations exceed certain permissible levels. In this work, the direct determination of some trace heavy metals in the drinking water were carried out by differential pulse anodic stripping voltammetry (DPASV). 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 the drinking 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, EPA and SASO.

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1.Introduction:

Human health can be affected by the quality of the food and drink that we take. Water intended for human consumption must be free from organisms and from concentrations of chemical substances that may be hazardous to health. Recent studies show that the levels of trace elements present in drinking water could seriously affect human health (Maroof *et al.*, 1990, Moukarzel *et al.*, 1992). World Health Organization (WHO) places great emphasis on the quality of drinking water and has recommended upper limits for a number of trace elements for drinking water (World *et al.*, 1977, World *et al.*, 1980).

This study was directed to measure concentrations of Zinc, Chromium and Cadmium in the commercially available drinking water in Makkah and Jeddah cities using Atomic Absorption Spectrometry technique. A total of 94 water samples were analyzed. The mean concentrations of the metals obtained in this study are within the maximum permissible levels for the drinking water recommended by the World Health Organization (WHO) and Saudi Arabian Standard Organization (SASO). Conductivity and pH of the water samples were also measured to investigate correlation between their values and the concentrations of the three metals. A positive correlation is obtained between the metal concentrations and the corresponding conductivity values, while no significant correlation is seen between the pH values and the metal concentrations (Tayyeb *et al.*, 2000).

Several techniques have been used in trace metal analysis with varying degrees of success and convenience. These techniques include UV-visible spectrophotometry, flame atomic absorption spectrometry (Eaton *et al.*, 1995), electrothermal atomic absorption spectrometry (percelay *et al.*,

1988), inductively coupled plasma atomic emission spectrometry (Eaton *et al.*, 1995), total reflection X-ray fluorescence spectrometry (Mukhtar *et al.*, 1991) and electrochemical stripping analysis (Adeloju *et al.*, 1996). Among the various techniques, stripping analysis offers the advantages of species characterization and of utilizing inexpensive instrumentation and low operating cost. When compared with other spectrometric methods, only electrothermal atomic absorption spectrometry has nearly the same sensitivity but is more expensive. The instrument for stripping analysis is small in size, has very low power demand, and requires no special installation such as cooling or ventilation. These features make stripping analysis suitable for in situ measurement (at which contamination or sample loss from adhesion to sample bottle during storage and transport can be minimized). None of the other techniques for trace metal quantitation can compete with stripping analysis on the basis of sensitivity per money invested (Wang *et al.*, 1985).

2. Materials and methods

Gathering samples Drinking water samples were chosen from The villages in Jazan region, Al-amria, Al-orooj, Zabart-Rashid and Bani-Malik villages. 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 drinking water elements was used by the consumers.

The apparatus used in the study:

The concentration of trace elements were measured by Polarograph 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. 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: Jizan Region suffers from a shortage of water that is reflected negatively on the citizen's health as a direct result of usage of filtered water and wells. 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). In this work, the direct

determination of some trace heavy metals in the drinking water were carried out by differential pulse anodic stripping voltammetry (DPASV) technique in Jazan region, Al-amria, Al-orooj, Zabart-Rashid and Bani-Malik villages.

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

In this study, the concentration of Zn trace element in drinking water was successfully determined by ASV technique. DPAS voltammograms of Zn element obtained from standard addition technique are given in Fig. 1. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation (Fig. 2). (Used voltammetric apparatus on quantitative mode 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.

As can be seen from the Fig. 1, 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, the concentration of Zn(II) element in drinking water was found to be between 0.0105 - 0.016 mg/l.

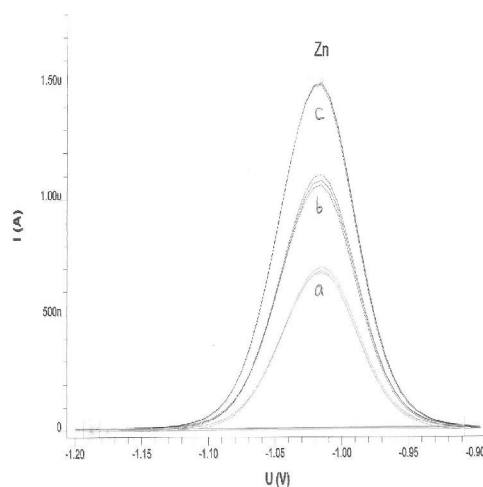


Figure 1. DPAS voltammograms of the Zn element obtained from standard addition technique a) 1 ml acetate buffer (pH = 4.2) + 10 ml drinking water. b) a + 100 μ l. c) b + 100 μ l standard solution of Zn (10 mg/l).

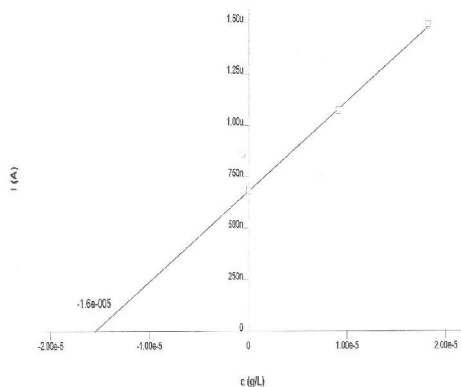


Figure 2. The calibration plot of Zn(II) element obtained from standard addition by DPASV technique.

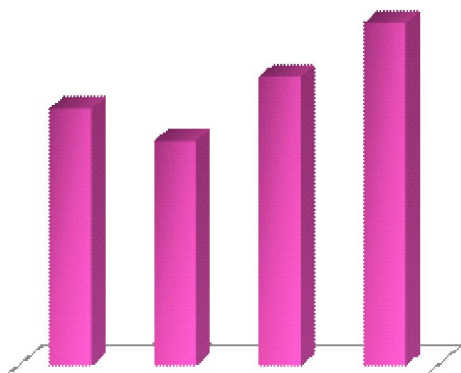


Figure 3. Concentration of Zn element in some village of Jazan region.

Also the study approved that the highest concentration of Zn element was found Al-Amria village drinking water which reached (0.016 mg/l) then Zabart-Rashid village drinking water reached to (0.0135 mg/l), then Al-Orooj village drinking water reached to (0.0120 mg/l) finally Bani - Malik village drinking water reached to (0.0105 mg/l), figure 3.

This value is between the limit values suggested by WHO, EPA and SASO. In addition, the concentration of Zn(II) element found indicates to be "the first quality water" of the drinking water according to the inland water quality classification consequently, it is understood that the concentration of Zn(II) in drinking water have no influence on the human health.

Also, the analysis has been determined without the interferences in the applied voltammetric

method. The advantages of the proposed voltammetric method over the other known techniques were sample preparation, sensitivity, rapidity and cost.

II- Determination of Lead (Pb) trace elements in drinking water sample: In this study, the concentration of Pb trace element in drinking water was successfully determined by ASV technique. DPAS voltammograms of Pb element obtained from standard addition technique are given in Fig 4. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation (Fig 5). (Used voltammetric apparatus on quantitative mode 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.

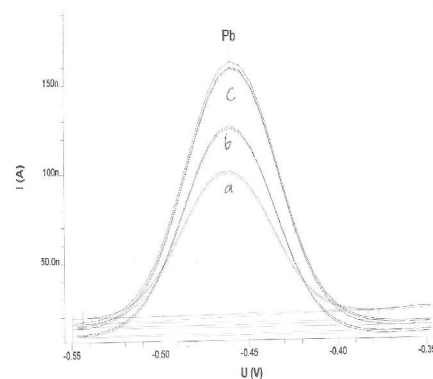


Figure 4. DPAS voltammograms of the Pb element obtained from standard addition technique a) 1 ml acetate buffer (pH = 4.2) + 10 ml drinking water. b) a + 100 μ l. c) b + 100 μ l standard solution of Pb (10 mg /l).

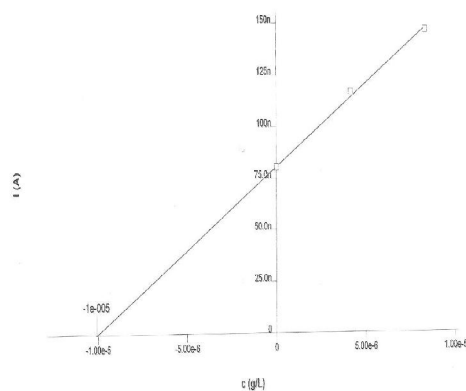


Figure 5. The calibration plot of Pb (II) element obtained from standard addition by DPASV technique.

As can be seen from the Fig. 4, 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, the concentration of Pb(II) element in drinking water was found to be between (0.0085 - 0.0365) mg/l.

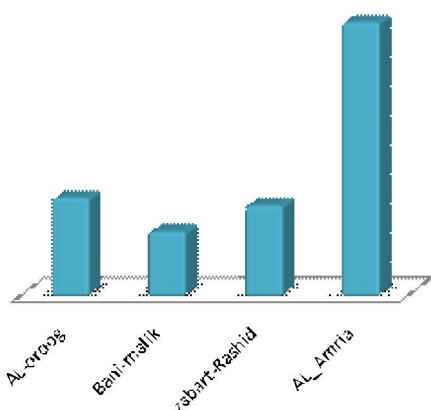


Figure 6. Concentration of Pb element in some village of Jazan region.

The highest concentration was found with Pb element noticed is (0.0365 mg/l) in Al-Amria drinking water village, while Bani-Malik village has the lower concentration it reached (0.0085mg/l) figure 6; the order is:

Al-Amria village > Al-Orooj village > Zabart- Rashid village > Bani-Malik village .

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

III- Determination of Cadmium (Cd) trace elements in drinking water sample:

In this study, the concentration of Cd trace element in drinking water was successfully determined by ASV technique. DPAS voltammograms of Cd element obtained from standard addition technique are given in Fig 7. The sensitivity was calibrated by standard additions to the sample and the initial metal concentrations were calculated by extrapolation (Fig. 8). (Used voltammetric apparatus on quantitative mode 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.

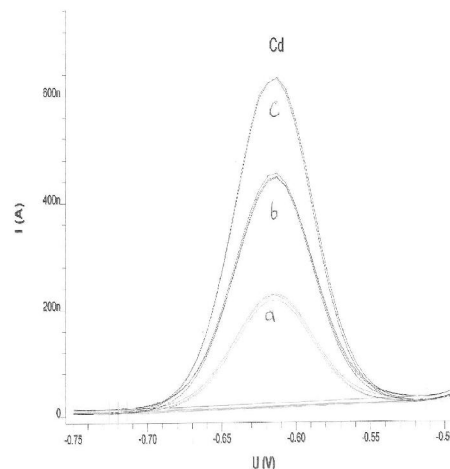


Figure 7. DPAS voltammograms of the Cd element obtained from standard addition technique. a) 1 ml acetate buffer (pH = 4.2)+10 ml drinking water. b) a+100 μ l. c) b+100 μ l standard solution of Cd (10 mg /l).

As can be seen from the Fig. 7, 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 tampon was determined to be 4.2. Under these conditions, the concentration of Cd(II) element in drinking water was found to be between 0.001 - 0.003 mg/l .

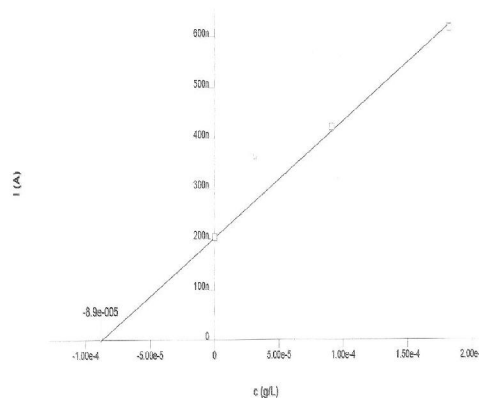


Figure 8. The calibration plot of Cd (II) element Obtained from standard addition by DPASV technique.

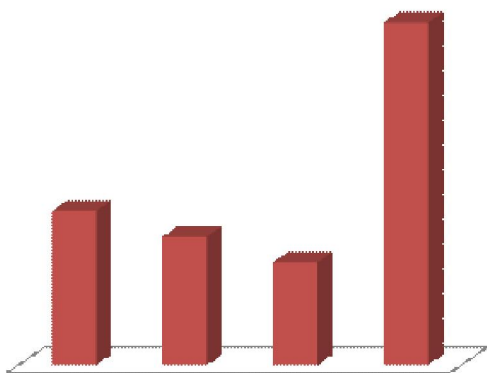


Figure 9. Concentration of Cd element in some village of Jazan region.

Also the study showed that the highest concentration Cd element was in Al-Amria drinking water (0.004 mg/l) then Al-Orooj village drinking water where (0.0018 mg/l), then Bani-Malik village drinking water (0.0015 mg/l) then Zabart- Rashid village drinking water (0.0012 mg/l) figure 9 .

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

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

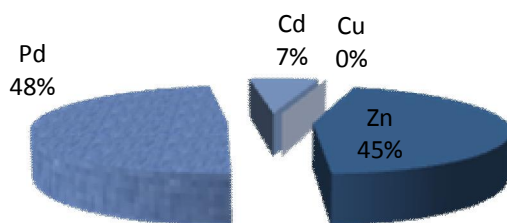


Figure 10 . Concentration of trace elements in AL-Orooj village

1. *Al-Orooj village drinking water*: figure 10, show the highest concentration Pb element is found ,that it reached to (0.013 mg/l) where the less concentration was Cu element , that it reached to (0.0 mg/l) . Zn element reached to (0.012 mg/l) , following that ,Cd element where it reached (0.0018 mg/l).

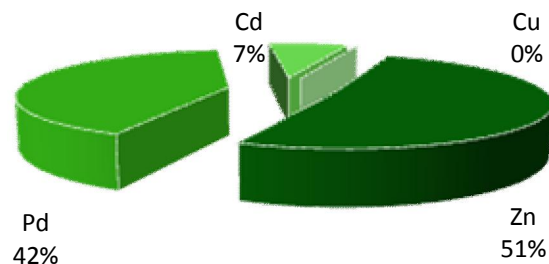


Figure 11. Concentration of trace elements in Bani-Malik village.

2. *Bani-Malik village drinking water* concerning Cu element, it was the lowest concentration within (0.0 mg/l) following that Cd element within (0.0015 mg/l) after that Pb element within (0.0085 mg/l) and the highest concentration was Zn element within (0.0105 mg/l) figure 11 .

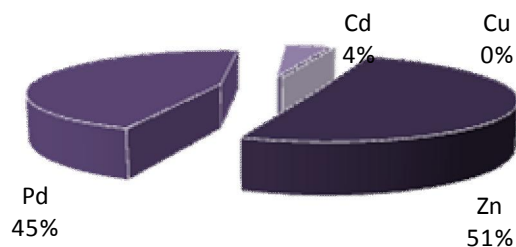


Figure 12. Concentration of trace elements in Zabart-Rashid village

3. *Zabart- Rashid village drinking water*, in that the highest concentration Zn element was within (0.0135 mg/l) , and it was lower in concentration Cu element within (0.0 mg/l) , and Pb element concentration reached to (0.012 mg/l) while Cd element concentration reached to (0.0012 mg/l) figure 12.

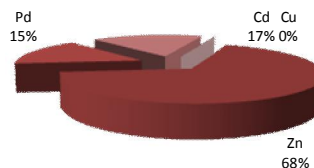


Figure 13. Concentration of trace elements in Al-Amria village

4. *Al-Amria village drinking water* concerning Zn element within (0.016 mg/l) and Cd element concentration reached to (0.004 mg/l) while the lowest concentration was in Cu element where it reached to (0.0 mg/l) and the highest concentration was Pb element within (0.0365 mg/l) figure 13.

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